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IMPROVED THERMAL BATTERY.(U)
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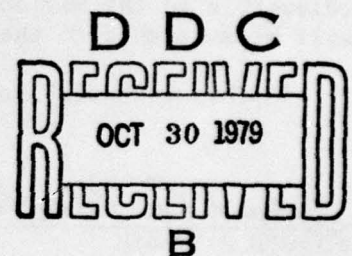
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IMPROVED THERMAL BATTERY

Praful V. Dand and Khushrow K. Press
KDI SCORE, INC.
Cockeysville, Maryland 21030



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WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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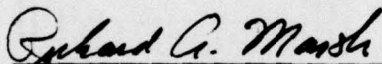
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This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.



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20. ABSTRACT (continued)

a superior system for thermal batteries, with longer life at high current densities, and greater energy density. Based on battery tests, it was concluded that calcium/calcium chromate thermal batteries could not achieve the goal of 30 minutes' life at 30 volts and 30 amperes, and that the lithium-aluminum/iron disulfide system, which achieved approximately 80% of the goal, could, with further development, reach and possibly surpass this goal.

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PREFACE

This report presents the work performed under U.S.A.F. Contract No. F33615-76-C-2144 to develop an improved thermal battery by advancing state-of-the-art technology to extend thermal battery capabilities for military applications. To meet the requirements of some systems which necessitate the use of more complicated and expensive reserve batteries, goals were set for 30 minutes' life, one second activation, voltage of 28 ± 2 volts, capacity of 15 ampere hours at 30 ampere discharge rate, 17 pounds weight and 140 cubic inches volume; with a target cost equal to or lower than present state-of-the-art thermal batteries.

An exhaustive study of the $\text{Ca/LiCl-KCl/CaCrO}_4$ system (which included investigation of the physical, chemical, and thermal properties of the components of the system) produced sufficient test data for determining composition, thickness, density, and configuration of the required pellet. Based on battery test results, it was determined that at 90 mA/cm^2 , a life of approximately 10 minutes could be projected, since the longest life attained was 5 minutes.

Investigation of a number of new electrochemical systems showed $\text{Li-Al/LiCl-KCl/FeS}_2$ to be a superior system, producing a life of over 35 minutes at 90 mA/cm^2 while providing an energy density of 248.9 Whr/kg, in single cell tests. In battery tests using the Li-Al/FeS_2 system, life of 24 minutes at 90 mA/cm^2 and energy density of 38.4 Whr/kg were achieved.

It is therefore concluded that the Li-Al/FeS_2 system is superior to the Ca/CaCrO_4 system as it exhibits very predictable performance at less cost, provides three to four times greater energy densities up to 1000 mA/cm^2 , is capable of providing longer battery lives at higher current densities, and it exhibits very low internal resistance and is therefore capable of sustaining very high current pulses (up to 2000 mA/cm^2).

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SECTION I

INTRODUCTION

Thermal batteries have always been desirable for military applications because of their long shelf life, high reliability, and relatively low cost. However, their use in long life (over 10 minutes) and high energy density applications has been limited because of the inherent characteristics of conventional electrochemical systems. The production, replacement, and maintenance costs, and lower reliability, of other primary, reserve batteries have been major factors in stimulating the demand for an improved thermal battery. Consequently, in June 1976, the United States Air Force Aeropropulsion Laboratories awarded KDI SCORE, Inc., a contract for Improved Thermal Batteries. The objectives of the program were advancement of the state-of-the-art through optimization of the calcium/calcium chromate system and investigation of new electrochemical systems. The program goal was to develop a 28 volt, 30 ampere battery to operate for thirty minutes.

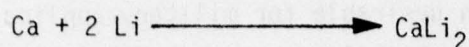
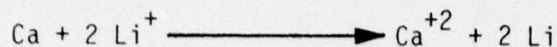
Thermal batteries are non-rechargeable, electrochemical power sources employing molten salt electrolytes that are solid and non-conductive at normal ambient temperatures. A pyrotechnic source within the battery, when ignited, provides sufficient heat to melt the electrolyte and raise the temperature to a desired operating level. Electrical energy can then be drawn from the system. Various electrochemical systems and cell constructions used in thermal batteries have been described in detail by R. Jasinski (High Energy Density Batteries, Plenum Press, New York. 1967), and N. C. Cahoon and G. W. Heise (The Primary Battery, John E. Wiley & Sons, New York. 1976).

The conventional systems have provided low energy density batteries for short life applications (less than 200 seconds) at moderate current drains. If longer life was required, batteries had to be designed for operation at low current density, thus increasing their size and weight. The $\text{Ca/LiCl-KCl/CaCrO}_4$ system has enjoyed the widest application due to several properties which are generally regarded as superior to those of the other systems.

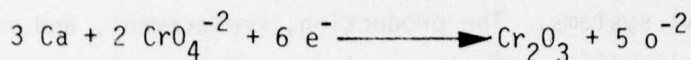
Long life (60 minutes) batteries have been developed (A. R. Baldwin, "A Sixty Minute Thermal Battery", Proceedings, 27th Power Sources Symposium. 1976) using the Ca/CaCrO_4 system operating at very low current density (15 mA/

cm²) and providing low energy density. However, this system has inherent problems which are evident from its cell reactions:

at the anode:



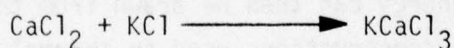
at the cathode:



The overall reaction, as postulated by Cahoon and Heise (cited above) is:



The formation of the complex compounds has been proved by P. F. Hlava and T. J. Headley ("Thermal Battery Reaction Products: Characterization by Electron Microprobe X-Ray Analyzer and Transmission Electron Microscope", SAND77-1317, Sandia Laboratories, Albuquerque, New Mexico. 1977). At low current density, formation of the CaLi₂ alloy (mp 230°C) at the anode-electrolyte interface sometimes causes serious voltage fluctuations (noise) and occasional cell dropouts. This causes the reliability of the batteries to be suspect. At high current density, the formation of the double salt, KCaCl₃ (mp 485°C), at the interface, per the reaction:



increases internal resistance and thereby reduces life.

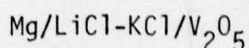
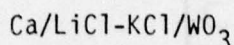
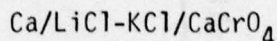
Based on literature search, it was assumed that thermal life of well over 30 minutes could be obtained from thermal batteries using adequate insulation. Preliminary calculations revealed that with the Ca/LiCl-KCl/CaCrO₄ system, one could drain 30 amperes from a battery using three paralleled stacks of twelve 120 mm OD cells. This would provide the required 28 ± 4 volts regulation at a current density of about 90 mA/cm². However, from the battery tests, it was concluded that this system was unable to provide the requisite performance. At 90 mA/cm² the best life obtained by a 10 cell battery, S/N P-17 (61 mm OD cells) was under 5 minutes.

A detailed study of Ca/LiCl-KCl/CaCrO₄ is discussed in Appendix D, including single cell and battery test results. From these results it was concluded that other systems would have to be investigated in order to

obtain the long life and high energy density desired for the final design of the battery.

In the past, various electrolyte, anode, and cathode materials have been investigated and suggested, but very few proved practical as thermal battery systems within the framework of existing technology.

The three systems which have found the broadest practical use in military hardware to the present time are:

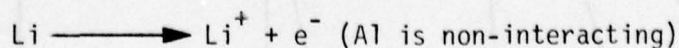


Alternate electrochemical couples utilizing calcium, magnesium, and a lithium-aluminum alloy were evaluated as anodes against various cathodic materials. The latter included calcium chromate, metal sulfides, metal oxides (CuO , Fe_2O_3 , NiO , V_2O_5 , and WO_3), and cupric chloride. A common electrolyte, the eutectic mixture of lithium chloride and potassium chloride, was used with all couples. Some typical voltage versus time plots are given in Figure 1 at a current density of 90 mA/cm^2 .

At the above current density, the advantages of the Li-Al/FeS_2 couple become immediately apparent. Its life of 35 minutes is almost three times that of the Ca/CaCrO_4 system. However, because the cell is heavier and provides a lower peak voltage, the energy density (248.9 Whr/kg) is only twice as great. Life as long as 100 minutes has been observed at a current density of 20 mA/cm^2 . The $\text{Ca/Fe}_2\text{O}_3$, Ca/FeS_2 , and Ca/CuO systems provided surprisingly good lives, voltages, and energy densities.

There is no inherent problem with the Li-Al/FeS_2 system as there is with the $\text{Ca/LiCl-KCl/CaCrO}_4$ system. The cell reactions as postulated by R. K. Steunenbergh ("Lithium-Aluminum/Metal Sulfide Batteries", Argonne National Laboratory, Illinois. 1977), are:

at the anode:



at the cathode:



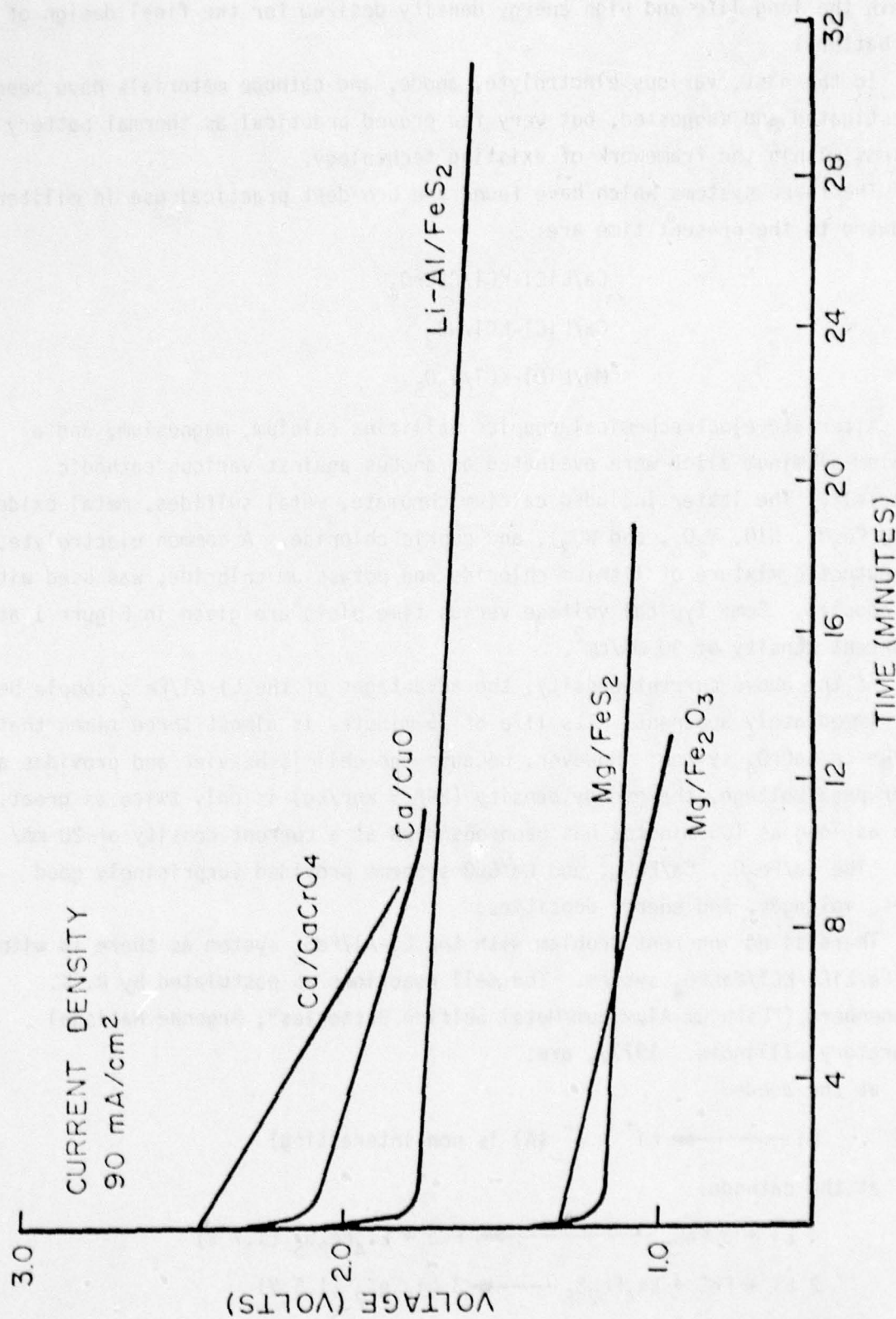
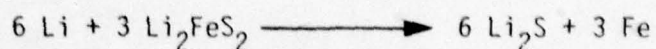
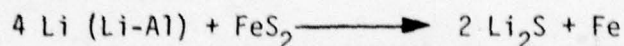


Figure 1. Single Cell Test Curves for Various Systems



The simplified total cell reaction is:



In this system, a low melting alloy is not necessary for the cell to perform and the complex compounds present do not seem to change the internal resistance. Another major advantage is that the solubility of FeS_2 in LiCl-KCl is lower than that of CaCrO_4 , thus reducing side reactions which are responsible for thermal runaways and reduction of capacity.

The performance characteristics of the two systems are compared in detail in later sections.

BATTERY TESTS

Batteries, 75 mm in diameter, using ten 61 mm diameter cells, were built for both the Ca/CaCrO_4 and the Li-Al/FeS_2 systems. These batteries were tested at -40°C , $+23^\circ\text{C}$, and $+74^\circ\text{C}$, at 90 mA/cm^2 current drain. Typical data for optimized batteries of both types are plotted in Figure 2. Although identical insulation was used in both types, the batteries containing Li-Al/FeS_2 provided considerably better performance (23.5 minutes, S/N P-161) than those using the Ca/CaCrO_4 system (5 minutes, S/N P-17).

Several batteries were also tested at current densities other than 90 mA/cm^2 , in the range of 50 to 800 mA/cm^2 . These units were fired at room temperature. Life versus current density data for the two systems are compared in Figure 3. The Li-Al/FeS_2 system performed two to four times better than the Ca/CaCrO_4 system at current densities higher than 50 mA/cm^2 . At lower current densities, the two systems seem to approach each other. It was also observed that there was no noise or appreciable change in the capacity of the Li-Al/FeS_2 system at various current densities.

The best energy density of 38.4 Whr/kg (70% of the goal) based on the stack weight (including active and non-active material) was supplied by a two-stack battery, S/N P-154, using the $\text{Li-Al/LiCl-KCl/FeS}_2$ system. The longest life of 23.5 minutes (78% of the goal) was exhibited by battery S/N P-161 at 90 mA/cm^2 using the same system in a single stack. The results are given in Table 1. The $\text{Ca/LiCl-KCl/CaCrO}_4$ system exhibited very poor performance and hence was unsuitable. Unlike the latter, the energy density improved by almost

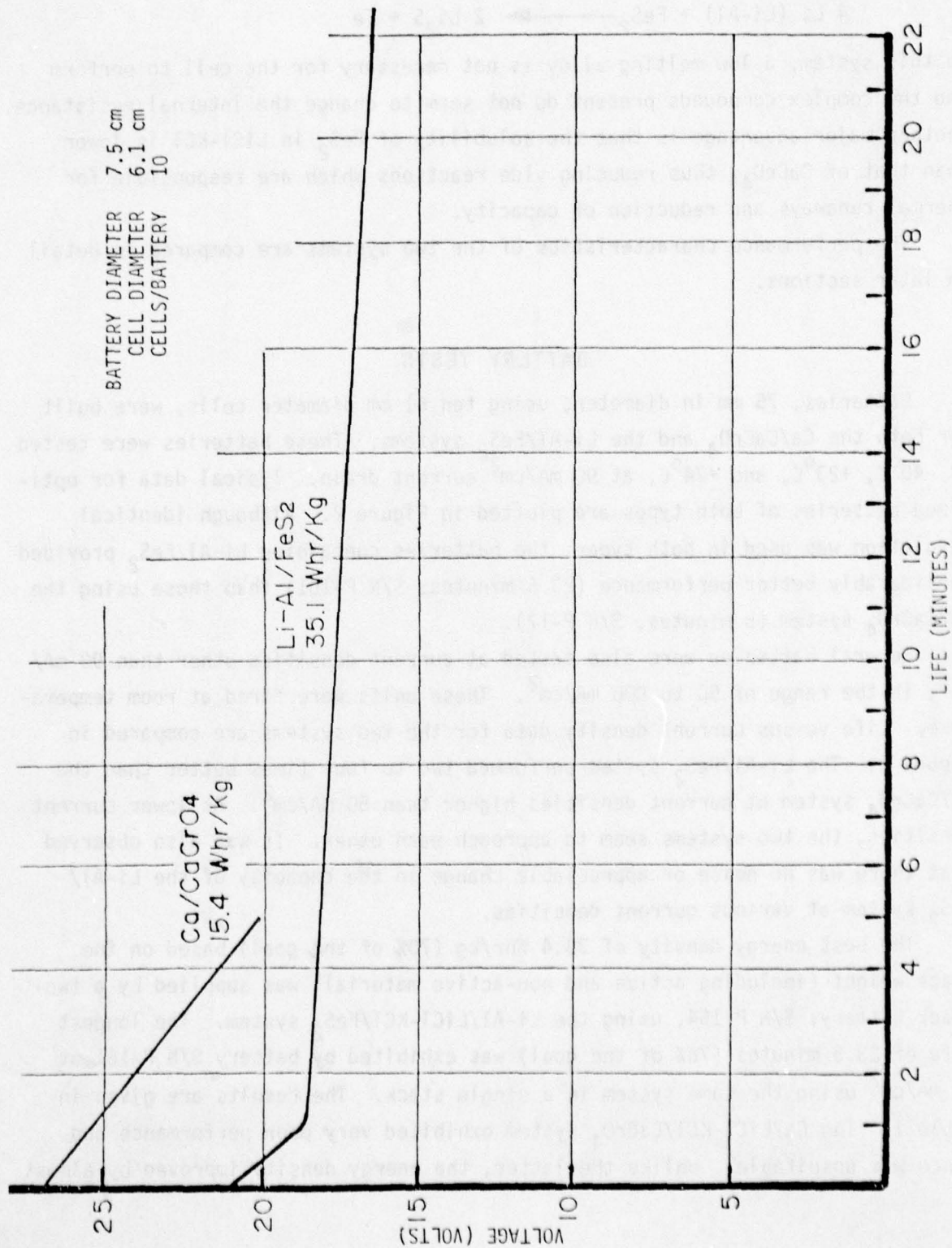


Figure 2. Comparison of Battery Life at 90 mA/cm²

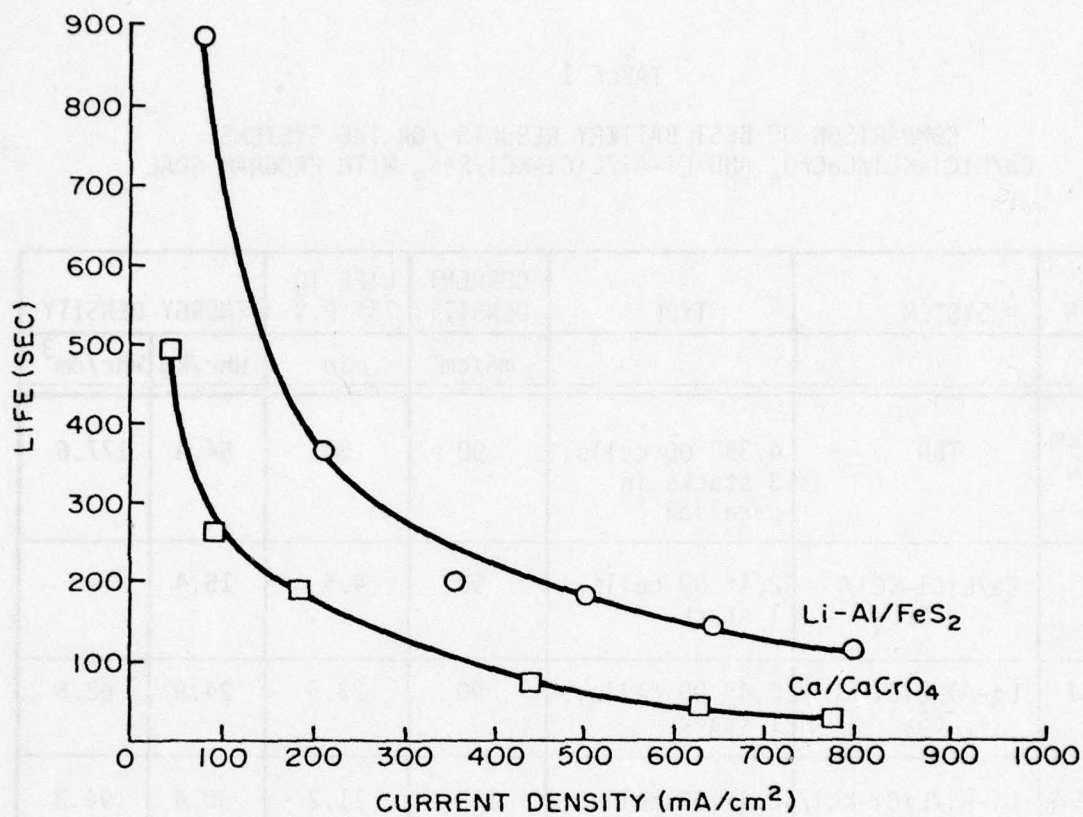


Figure 3. Comparison of Battery Life at Different Current Densities for Ca/CaCrO₄ and Li-Al/FeS₂

TABLE 1

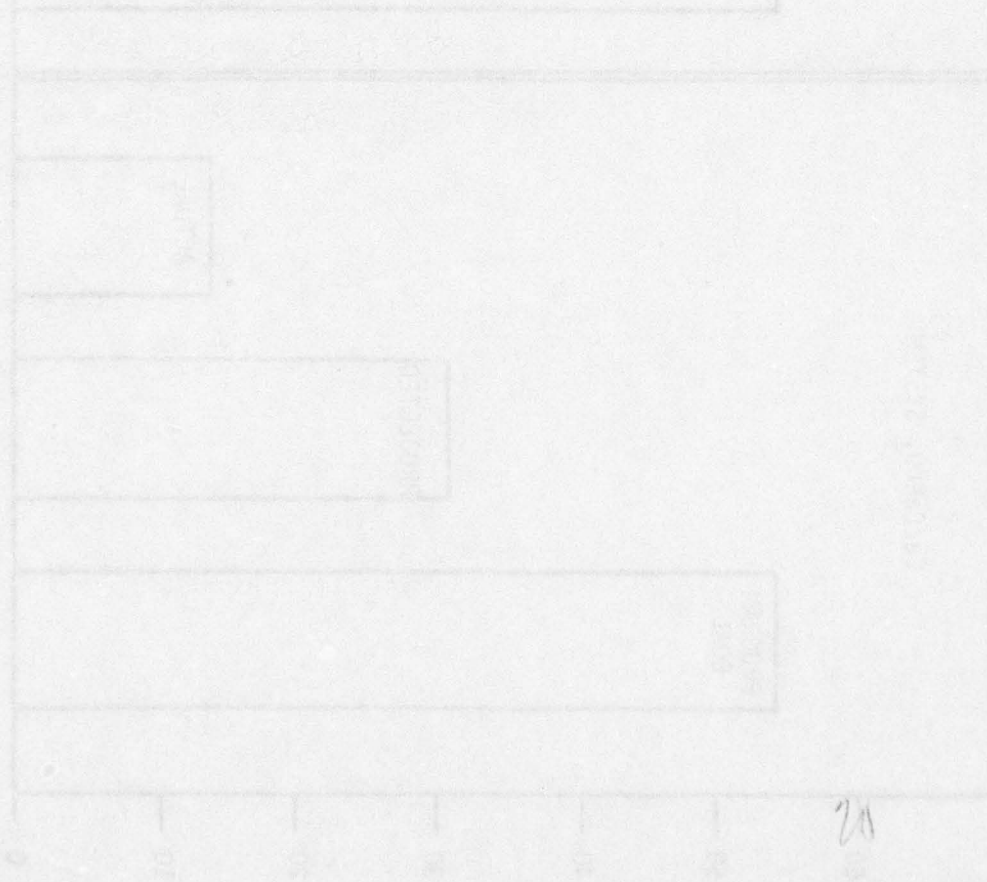
COMPARISON OF BEST BATTERY RESULTS FOR THE SYSTEMS
 $\text{Ca/LiCl-KCl/CaCrO}_4$ AND $\text{Li-Al/LiCl-KCl/FeS}_2$ WITH PROGRAM GOAL

S/N	SYSTEM	TYPE	CURRENT DENSITY	LIFE TO 75% P.V.	ENERGY DENSITY	
			mA/cm^2	min	Whr/kg	Whr/dm^3
Program Goal	TBD	4.35" OD cells, 3 stacks in parallel	90	30	54.4	177.6
P-17	$\text{Ca/LiCl-KCl/CaCrO}_4$	2.4" OD cells, 1 stack	90	4.5	15.4	-
P-161	$\text{Li-Al/LiCl-KCl/FeS}_2$	2.4" OD cells, 1 stack	90	23.5	24.8	63.5
P-154	$\text{Li-Al/LiCl-KCl/FeS}_2$	2.4" OD cells, 2 stacks in parallel	150	11.2	38.4	94.3

50% over battery S/N P-161 (24.9 Whr/kg) by using two paralleled stacks. Battery S/N 125 (life to 75% peak voltage - 22.5 minutes, energy density - 35 Whr/kg) illustrates this. The specific energy density by volume was over 50% of the goal. Thus, a battery operating at 150 mA/cm^2 using the new system, would require only two stacks in parallel to supply the rated current.

It is estimated that the present state-of-the-art Li-Al/LiCl-KCl/FeS₂ system will provide a life of over 15 minutes at 30 amperes in the given 144 cubic inch envelope, and that it would weigh less than 17 pounds. Life of over 20 minutes could be obtained at 20 amperes with the same limitations. Given additional time and funds, it is believed that this system could be improved considerably, for more efficient operation and broader application.

Figure 4 gives a comparison of the program goal with our projected energy density with the two systems and the actual value obtained. As can be seen, Li-Al/FeS₂ has demonstrated capacity to provide 38.4 Whr/kg (70% of the program goal of 54.4 Whr/kg).



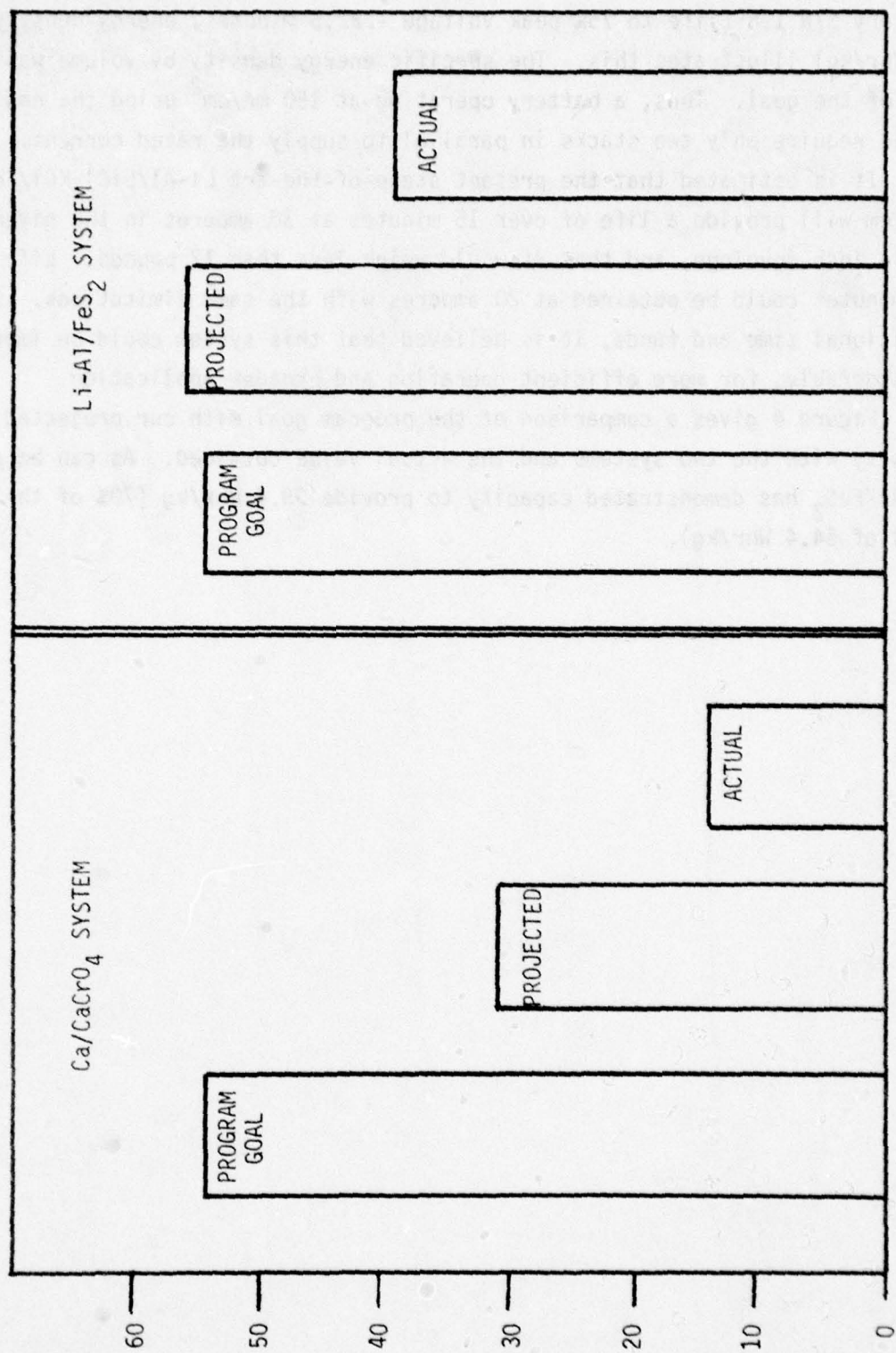


Figure 4. Comparison of Actual and Projected Energy Densities with Goal

SECTION II

ELECTROCHEMICAL STUDIES

A comprehensive study was conducted in an effort to optimize the performance of the $\text{Ca/LiCl-KCl/CaCrO}_4$ system by varying chemical composition and physical characteristics. A detailed discussion with results is given in Appendix D.

From the results, it was concluded that this system would not be able to meet the project goals and other systems would have to be developed to provide the necessary energy and life.

NON-STANDARD SYSTEMS

In an attempt to find an improved alternate electrochemical system for thermal batteries, various couples were tested at 50 mA/cm^2 , 90 mA/cm^2 , and 150 mA/cm^2 .

The following couples were investigated. In all cases LiCl-KCl eutectic mixture was used as electrolyte, unless otherwise stated.

Ca/CaCrO_4	$\text{Ca/Fe}_2\text{O}_3$
Li-Al/CaCrO_4	$\text{Li-Al/Fe}_2\text{O}_3$
Mg/CaCrO_4	$\text{Mg/Fe}_2\text{O}_3$
Ca/FeS_2	Ca/WO_3
Li-Al/FeS_2	Li-Al/WO_3
Mg/FeS_2	Mg/WO_3
$\text{Ca/V}_2\text{O}_5$	Ca/CuO
$\text{Li-Al/V}_2\text{O}_5$	Ca/NiO
$\text{Mg/V}_2\text{O}_5$	Ca/CuCl_2
Li-Al/CuCl_2 with NaAlCl_4 electrolyte	
Li-Al/FeCl_3 with NaAlCl_4 electrolyte	

Results of the tests are given in Tables 2, 3, and 4, respectively; corresponding voltage versus time curves for these systems are plotted in Figures 5,

6, and 7 respectively. Based on these results, the following observations are made:

- 1) Greatest energy density (245.7 Whr/kg) and longest life (62.5 minutes) were exhibited by the Li-Al/FeS₂ system at 50 mA/cm² (Table 2, Figure 5); its unit cell voltage under load is comparatively low. Li-Al/CaCrO₄ provided 179.4 Whr/kg and 20 minutes' life at 2.33 volts/cell peak, and Ca/CaCrO₄ provided 160.7 Whr/kg and 26 minutes' life at 2.51 volts/cell peak.
- 2) At 90 mA/cm² (Table 3, Figure 6), FeS₂ is superior as a cathode material to CaCrO₄ or other depolarizers tested. The energy densities were 248.9 Whr/kg and 141.92 Whr/kg, respectively, for Li-Al/FeS₂ and Ca/FeS₂, as compared to 98.08 Whr/kg for Li-Al/CaCrO₄ and 121.03 Whr/kg for Ca/CaCrO₄ systems.
- 3) At 150 mA/cm² (Table 4, Figure 7), Li-Al/FeS₂ is the best system with 264.7 Whr/kg and 21.0 minutes' life. Li-Al is the best anode when used with FeS₂, but Ca is the best anode when used with CaCrO₄, the latter yielding 154.11 Whr/kg, 8.3 minutes' life.
- 4) With all cathodes, Li-Al exhibits a peak voltage equal to or slightly lower than Ca and also provides noise-free performance except with WO₃.
- 5) If a short-life battery is required for a pulse load application and height is critical, the vanadium pentoxide cathode would be the best choice since it performs well with any anode.
- 6) Cupric chloride exhibited strange behavior; that is, a life of approximately 45 seconds was observed at all current densities with copper being deposited on the anode surface (Table 3, Figure 6).

Based on these results, it was concluded that the Li-Al/FeS₂ system was most suitable as an alternate electrochemical system capable of meeting the goal requirement.

TABLE 2

SINGLE CELL TEST RESULTS FOR VARIOUS SYSTEMS AT
AT 50 mA/cm² CURRENT DENSITY

SYSTEM	PEAK VOLTAGE	ACTIVE LIFE TO 75% P.V.	ENERGY DENSITY
	(Volts)	(Seconds)	(Whr/kg)
(1) Ca/LiCl-KCl/CaCrO ₄	2.51	1535	160.7
(2) Li-Al/LiCl-KCl/CaCrO ₄	2.33	1212	125.5
(3) Mg/LiCl-KCl/CaCrO ₄	1.62	546	45.1
(4) Ca/LiCl-KCl/FeS ₂	2.37	701	67.1
(5) Li-Al/LiCl-KCl/FeS ₂	2.17	3749	245.7
(6) Mg/LiCl-KCl/FeS ₂	1.57	2554	202.9
(7) Li-Al/LiCl-KCl/V ₂ O ₅	3.06	296	30.7
(8) Li-Al/LiCl-KCl/Fe ₂ O ₃	2.14	463	23.6
(9) Mg/LiCl-KCl/Fe ₂ O ₃	1.37	914	67.2
(10) Ca/LiCl-KCl/WO ₃	2.30	823	52.3
(11) Mg/LiCl-KCl/WO ₃	1.61	339	10.1

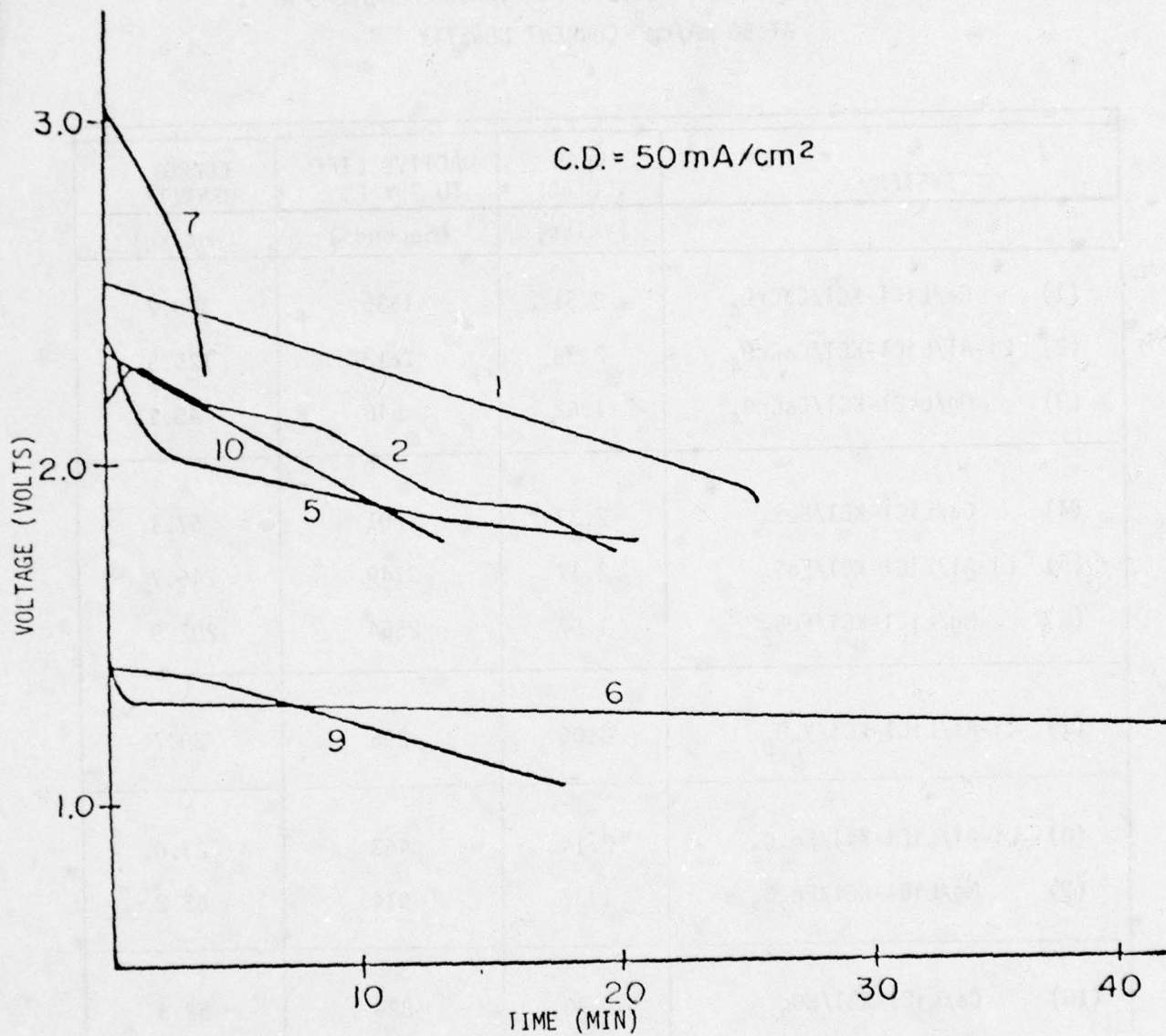


Figure 5. Typical Voltage Vs. Time Curves for Various Systems
(The Curve Numbers Correspond to Systems in Table 2)

TABLE 3

SINGLE CELL TEST RESULTS FOR VARIOUS SYSTEMS
AT 90 mA/cm² CURRENT DENSITY

SYSTEM	PEAK VOLTAGE	ACTIVE LIFE TO 75% P.V.	ENERGY DENSITY
	(Volts)	(Seconds)	(Whr/kg)
(1) Ca/LiCl-KCl/CaCrO ₄	2.38	643	121.0
(2) Li-Al/LiCl-KCl/CaCrO ₄	2.18	724	98.1
(3) Mg/LiCl-KCl/CaCrO ₄	1.44	318	41.5
(4) Ca/LiCl-KCl/FeS ₂	2.28	801	141.9
(5) Li-Al/LiCl-KCl/FeS ₂	2.05	2138	248.9
(6) Mg/LiCl-KCl/FeS ₂	1.46	1147	157.6
(7) Ca/LiCl-KCl/V ₂ O ₅	2.91	159	33.5
(8) Li-Al/LiCl-KCl/V ₂ O ₅	2.92	240	45.3
(9) Mg/LiCl-KCl/V ₂ O ₅	2.38	204	27.6
(10) Ca/LiCl-KCl/Fe ₂ O ₃	2.03	534	55.0
(11) Li-Al/LiCl-KCl/Fe ₂ O ₃	2.04	376	34.9
(12) Mg/LiCl-KCl/Fe ₂ O ₃	1.27	787	60.9
(13) Ca/LiCl-KCl/WO ₃	2.22	408	48.3
(14) Mg/LiCl-KCl/WO ₃	1.48	219	22.1
(15) Ca/LiCl-KCl/CuO	2.30	676	105.6
(16) Ca/LiCl-KCl/NiO	1.18	543	44.7
(17) Ca/LiCl-KCl/CuCl ₂	2.67	45	7.9

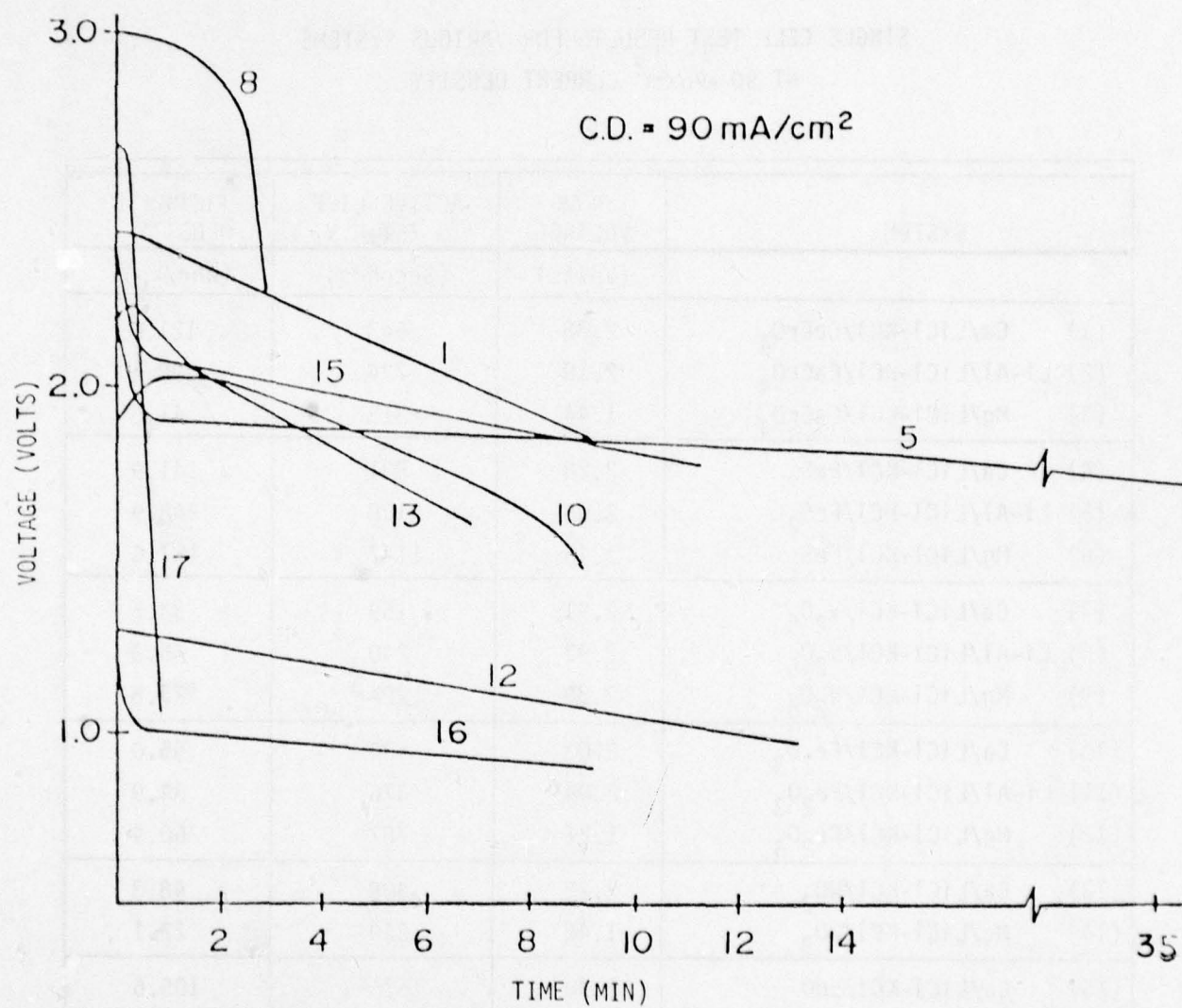


Figure 6. Typical Voltage Vs. Time Curves for Various Systems
(The Curve Numbers Correspond to Systems in Table 3)

TABLE 4

SINGLE CELL TEST RESULTS FOR VARIOUS SYSTEMS
AT 150 mA/cm² CURRENT DENSITY

SYSTEM	PEAK VOLTAGE	ACTIVE LIFE TO 75% P.V.	ENERGY DENSITY
	(Volts)	(Seconds)	(Whr/kg)
(1) Ca/LiCl-KCl/CaCrO ₄	2.30	497	154.1
(2) Li-Al/LiCl-KCl/CaCrO ₄	1.93	433	92.0
(3) Mg/LiCl-KCl/CaCrO ₄	1.18	146	25.6
(4) Ca/LiCl-KCl/FeS ₂	2.15	412	129.6
(5) Li-Al/LiCl-KCl/FeS ₂	1.95	1260	264.7
(6) Mg/LiCl-KCl/FeS ₂	1.28	457	97.1
(7) Ca/LiCl-KCl/Fe ₂ O ₃	1.93	235	41.3
(8) Li-Al/LiCl-KCl/Fe ₂ O ₃	1.86	196	30.2
(9) Ca/LiCl-KCl/WO ₃	2.08	210	43.2
(10) Mg/LiCl-KCl/WO ₃	1.30	100	24.8

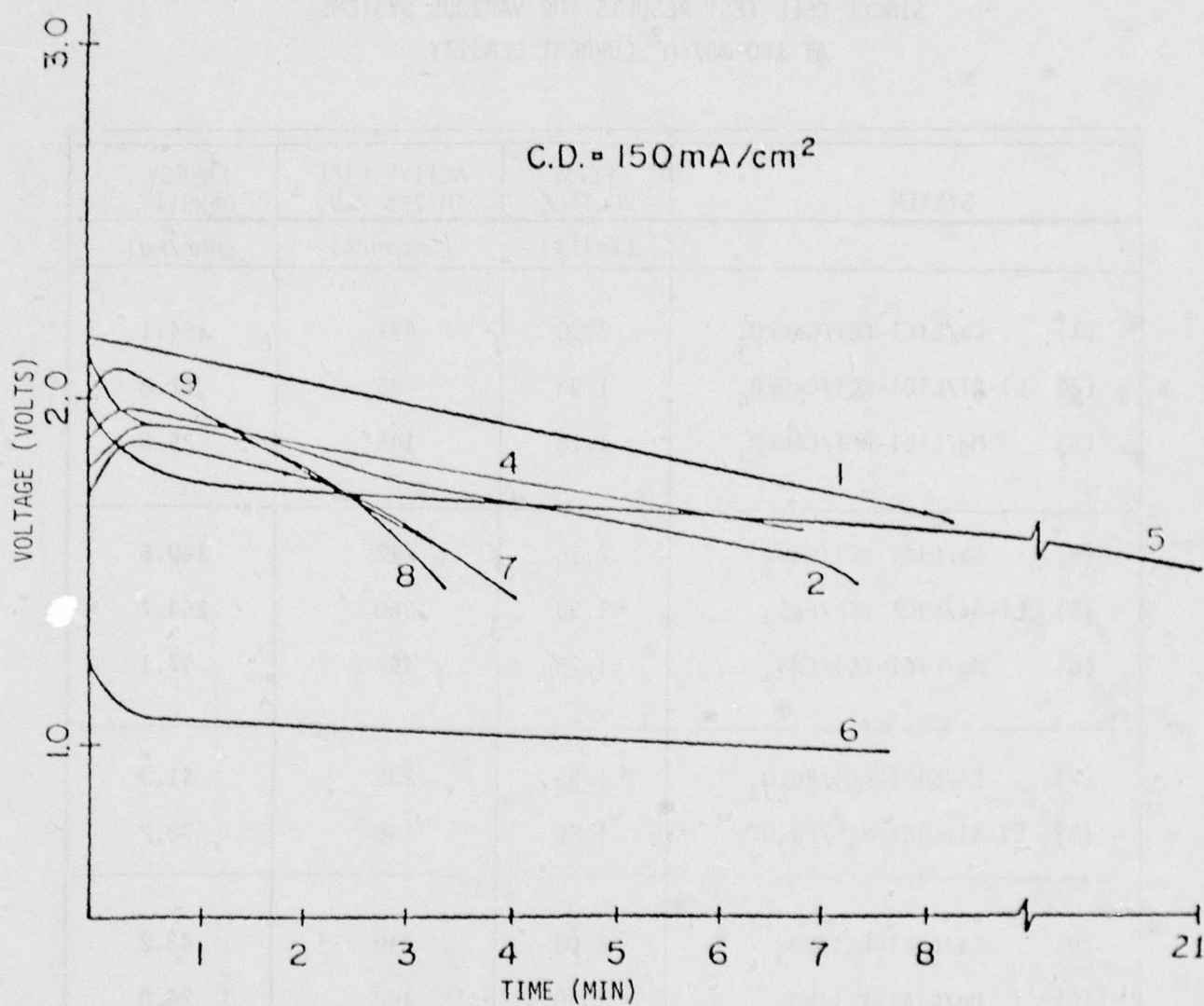


Figure 7. Typical Voltage Vs. Time Curves for Various Systems
(The Curve Numbers Correspond to Systems in Table 4)

DETAILED STUDY OF Li-Al/FeS₂ SYSTEM

A comprehensive study of Li-Al/FeS₂ system, feasible within the time frame, was conducted. This enabled us to optimize the system to a certain extent. Reproducible results exhibiting the potential of this system were obtained; however, considerable work remains to be done in completely defining and understanding the mechanism of the system. The important parameters that were evaluated in single cell tests (SCT) are discussed here. Whenever possible, a comparison is made with the Ca/CaCrO₄ system.

Chemical Composition of Depolarizer Layer (DE). Keeping the composition of the anode and electrolyte (EB) layers constant, the electrolyte/depolarizer (E/D) ratio in the catholyte (DE) layer was varied.

The single cell tests were run at 500°C, 0.4 kg/cm², and 90 mA/cm². The results, shown in Figure 8, indicate that an E/D ratio of 0.5 is optimum and that there is a critical amount of electrolyte required for the cathode to conduct satisfactorily. The effect of E/D ratio at different current densities is discussed in detail in Appendix D for the Ca/CaCrO₄ system.

Thickness. In Figure 9, life to 75% of peak voltage is plotted against the thickness of the DEB pellet for Ca/CaCrO₄ and against the thickness of the cathode (DE) layer for the Li-Al/FeS₂ system. In the latter, the anode and electrolyte layers were held constant at 0.81 mm and 0.25 mm, respectively. In all cases, the densities were kept constant and both systems were tested at the optimum temperature and pressure. From the graphs, it is observed that the life of the Ca/CaCrO₄ system does not increase substantially after 1.1 mm. However, the life of the Li-Al/FeS₂ shows a continued increase. This indicates that the specific conductivity of the disulfide cell is considerably higher and hence the intra-cell distance does not substantially affect performance.

Specific Conductance. In order to measure the specific conductance of each system, the internal resistance of the cell was measured by loading the cell at 90 mA/cm² and then opening the circuit (no load condition) every 50 seconds for a period of 0.2 second. Both ohmic and non-ohmic resistances were then included in the calculation of specific conductance. The measurement also includes cell contact resistance and the resistance between the current collectors and the cell. As expected from the thickness experiments, Figure 10 shows that the conductivity of the chromate system decreases with time. The flat behavior of the disulfide conductance suggests that the reaction products

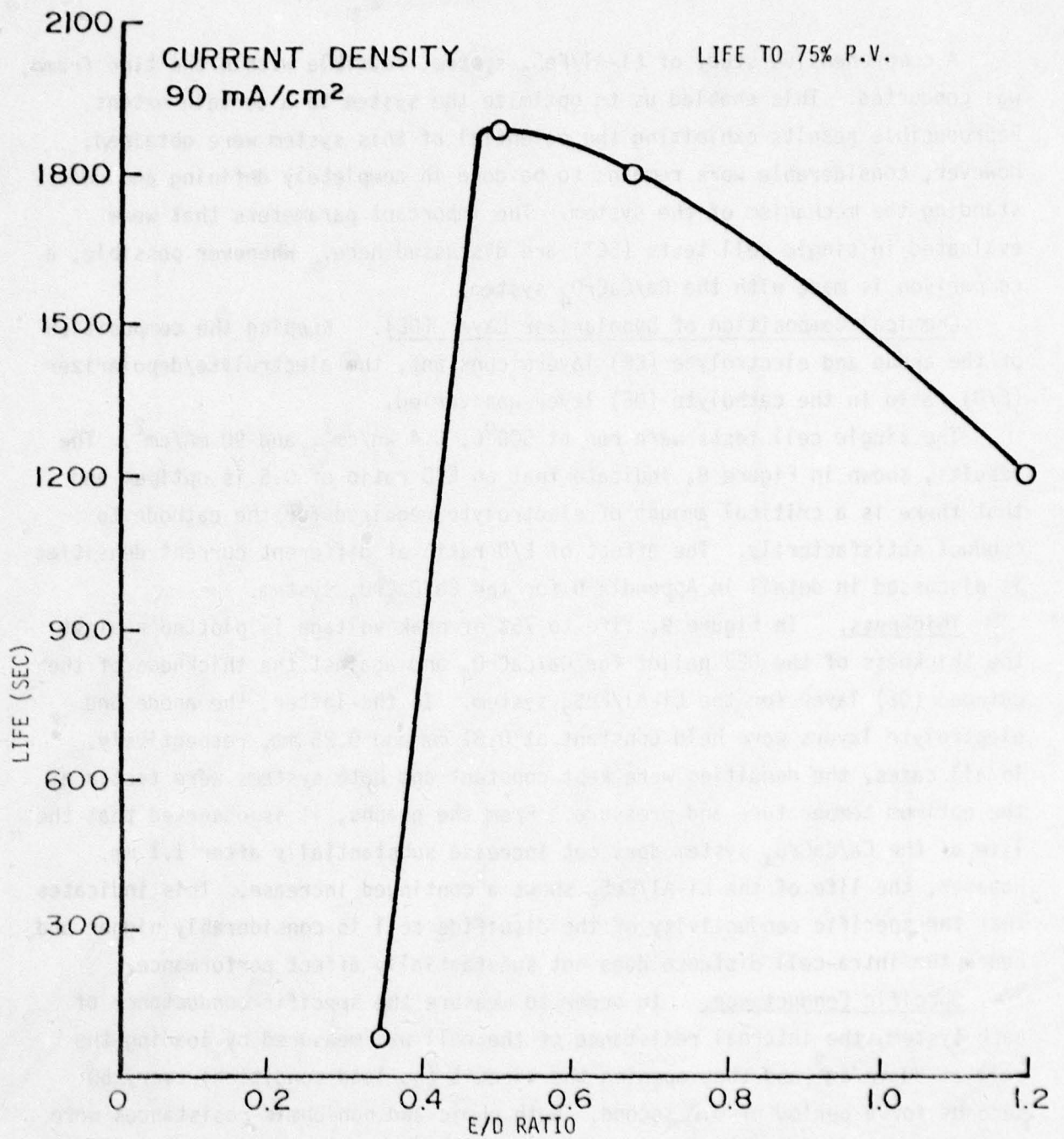


Figure 8. Effect of E/D Ratio in Catholyte Layer (DE) on Life in SCT for Li-Al/LiCl-KCl/FeS₂ System

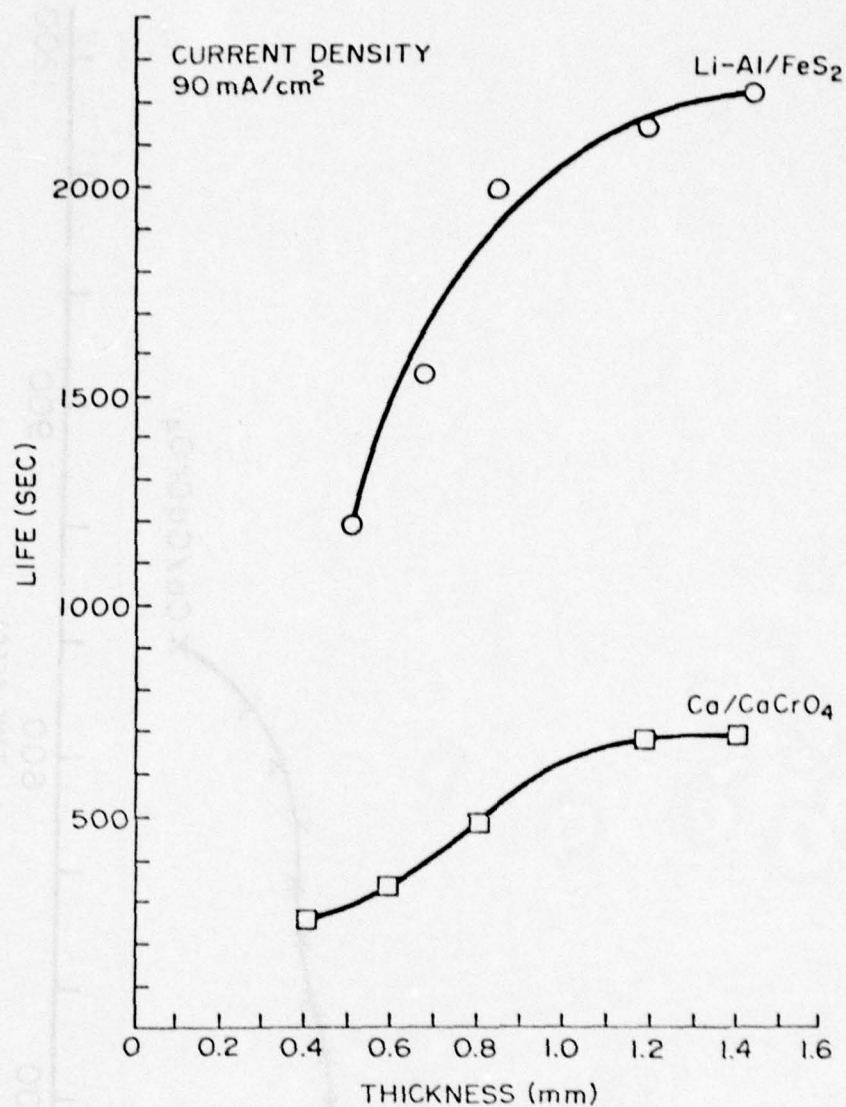


Figure 9. Effect of Thickness on Life for the Two Systems Ca/CaCrO₄ and Li-Al/FeS₂ in Single Cell Tests

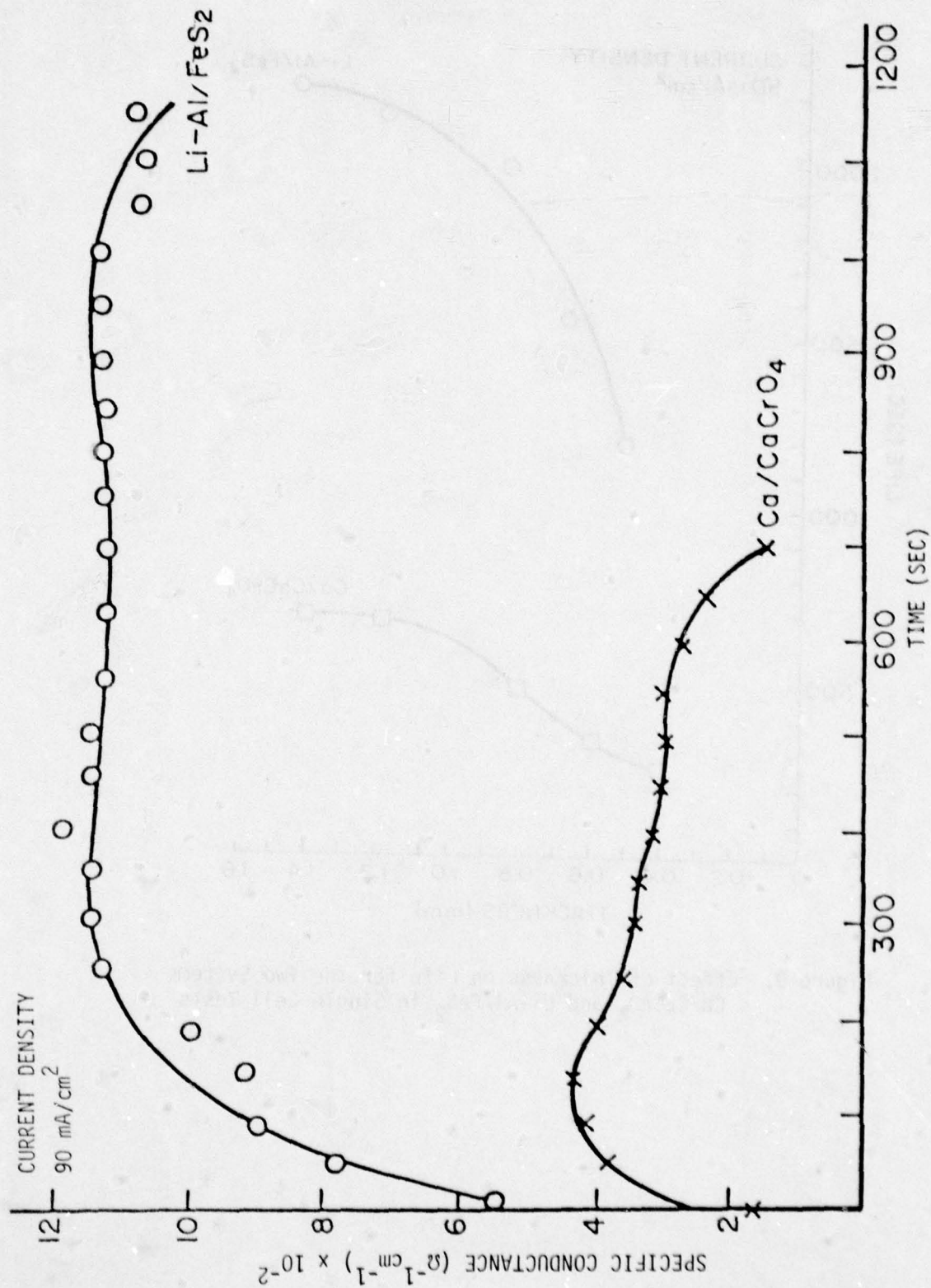


Figure 10. Change in Specific Conductance with Time in SCT for Li-Al/FeS₂ and Ca/CaCrO₄ Systems

are not deleterious to conductivity and that life is probably limited by concentration of one of the active materials.

Density. As with the study of pellet thickness, the density of the DE layer (FeS_2) and DEB layer (CaCrO_4) was varied, keeping all other parameters constant. The Ca/CaCrO_4 was found to be less susceptible to slight changes in pellet density (Figure 11) than the Li-Al/FeS_2 system which exhibited both a maximum and a minimum. To facilitate comparison of the two systems, the density is expressed as a percentage of the actual density of the depolarizer mix.

Particle Size. The DE powder mix for the Li-Al/FeS_2 system and the DEB powder mix for the Ca/CaCrO_4 system were first segregated into different particle size ranges and then pelletized. Cells using the two systems were then studied at 90 mA/cm^2 . The results are shown in Figure 12. It was observed that the Ca/CaCrO_4 system required a narrow range of particle sizes (120 to 160 microns) for maximum life. On the other hand, Li-Al/FeS_2 worked satisfactorily over a wider particle size range. In this study it was noted that along with the particle size separation there also occurred a chemical segregation. It is believed that the effect of this change in chemical composition is minor.

Temperature. The effect of operating temperature on cell life is critical in evaluating a new electrochemical system for use in thermal batteries since they must operate over a wide temperature range. To simulate battery temperatures, single cell tests were conducted between 400°C and 600°C . Two compositions of each system were evaluated. The Li-Al/FeS_2 system showed a greater stability with temperature change. Figure 13 also shows how this stability can be varied by changing the pellet composition. For the Ca/CaCrO_4 system, the cell performance is limited at the low temperatures by the freezing out of the double salt, KCaCl_3 , below 485°C and by the self-destructive chemical reaction between calcium and calcium chromate at temperatures above 580°C . There is no evidence that the products of reaction of the Li-Al/FeS_2 cell cause appreciable deterioration in performance. It is absolutely essential that the separator layer (EB) be used in the Li-Al/FeS_2 system as Li-Al in direct contact with the DE layer has exhibited highly exothermic reactions causing even the current collectors to melt. The two layer pellet prevents any such self-degrading chemical reaction.

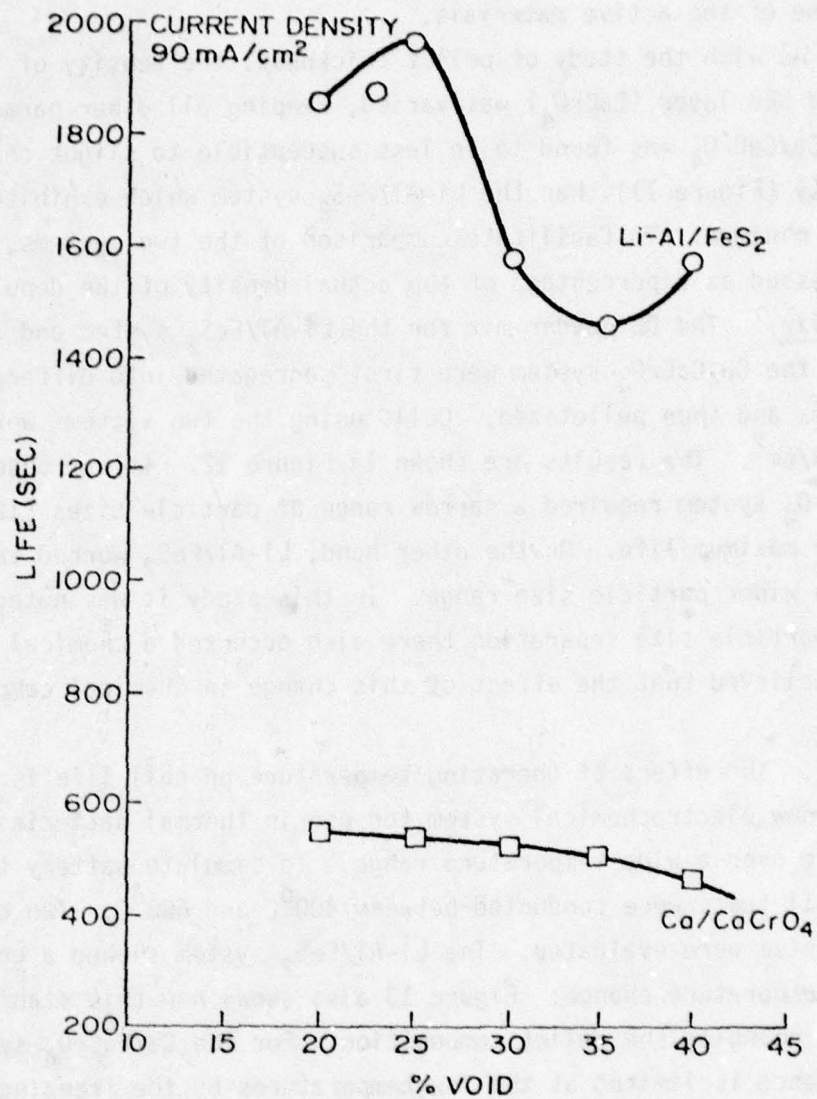


Figure 11. Effect of Density on Life for the Two Systems Ca/CaCrO₄ and Li-Al/FeS₂ in Single Cell Tests

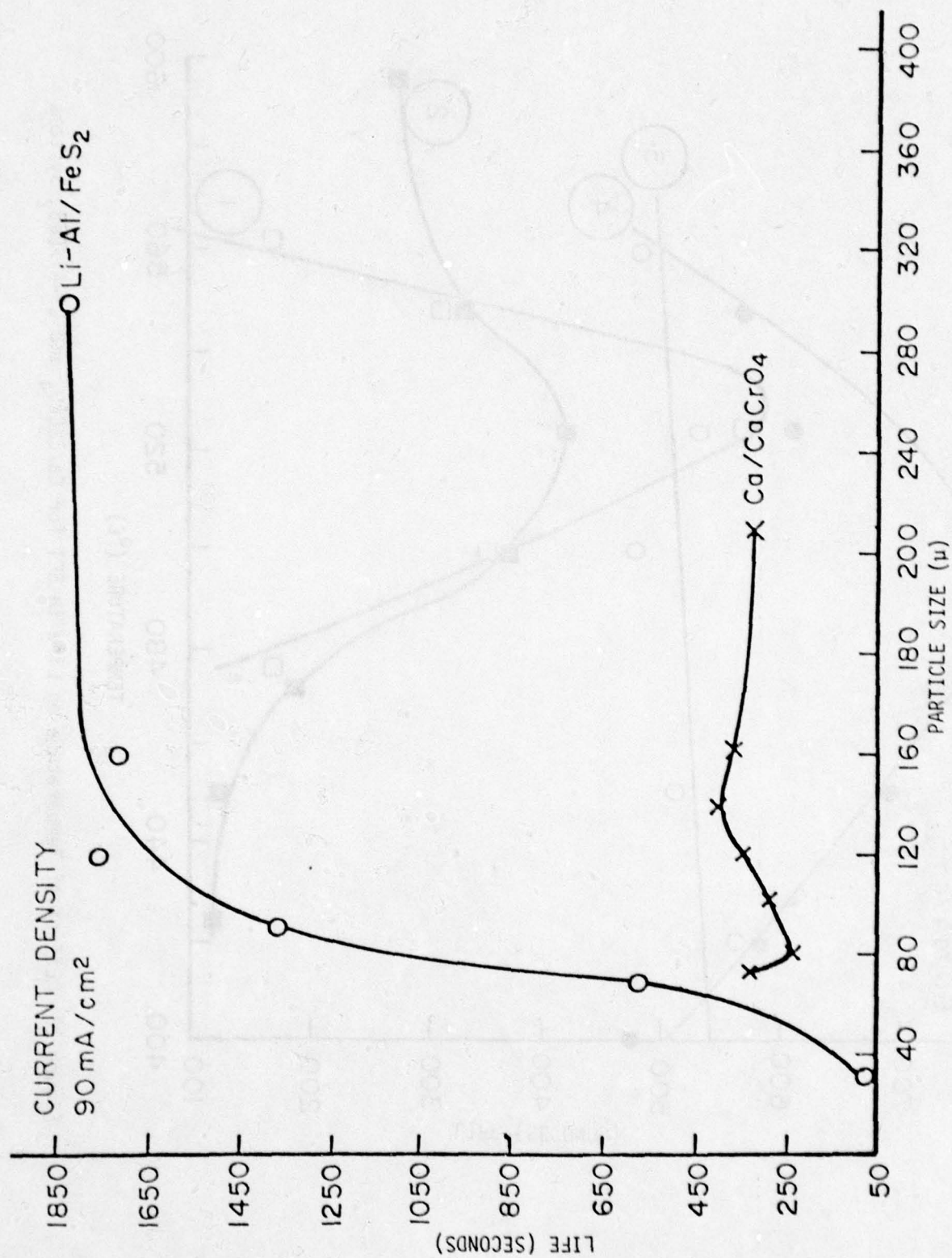


Figure 12. Effect of Particle Size on Life for the Two Systems Ca/CaCrO₄ and Li-Al/FeS₂ in SCT

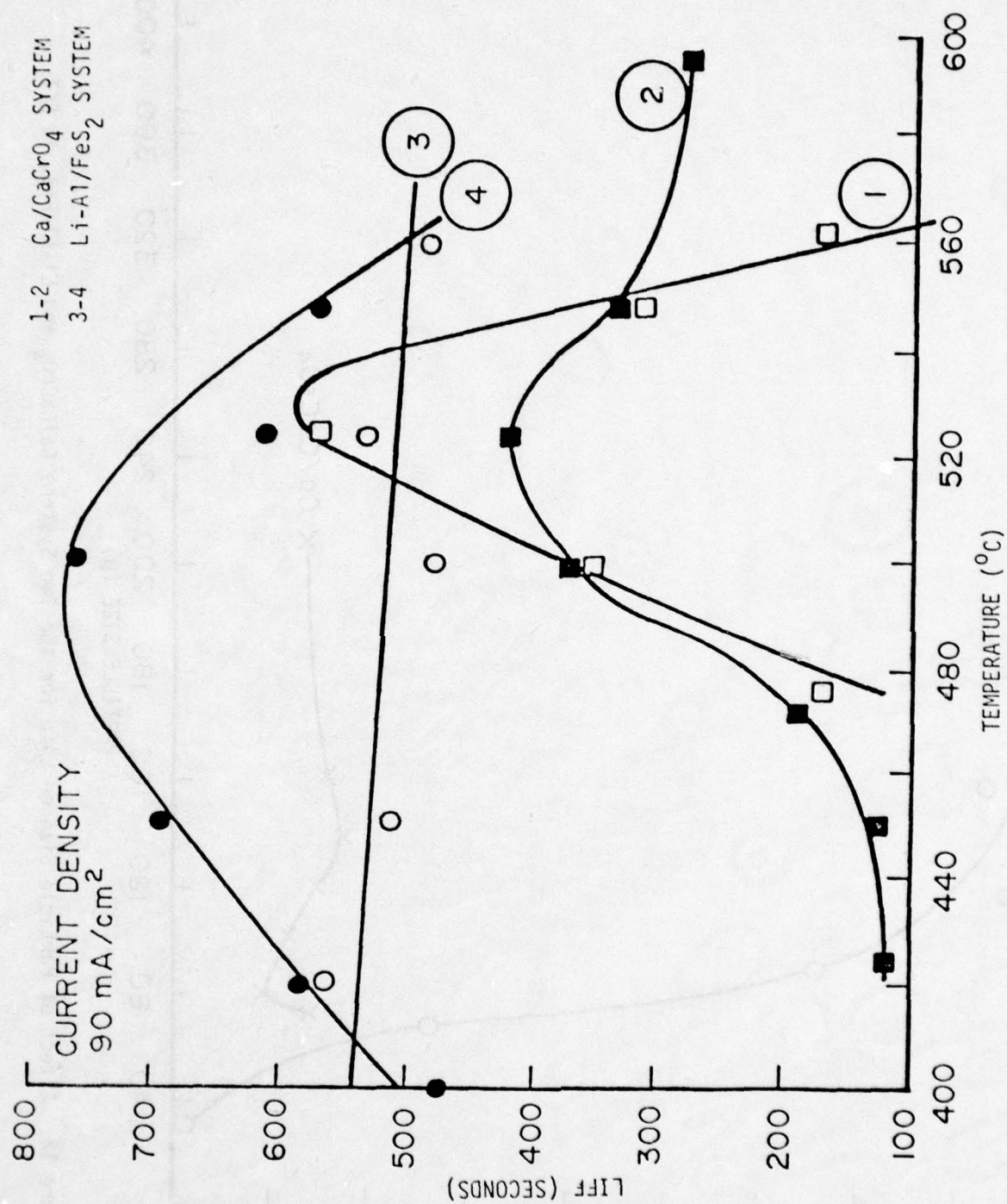


Figure 13. Effect of Temperature on Life in SCT for Ca/CaCrO₄ and Li-Al/FeS₂ Systems

Transient Peak. If the Li-Al/FeS₂ is not excessively thick (greater than 2.0 mm), and if the cell is not thermally pre-heated, a transient peak is observed on activation. The cell reaches about 2.05 volts and then drops rapidly to about 85-90% of its initial value in the first 30 seconds. It is suspected that this unpredictably high peak voltage is due to the presence of free sulphur in the pyrite, leading to the reaction



In order to prevent this transient condition, and thereby increase life to 80% of peak voltage, several experiments were conducted with limited success. These consisted of altering the entire cell by electrically shorting or thermally fusing these cells. As indicated in Table 8, physical additions to the cathode were also attempted. However, in all cases, the peak voltage was reduced substantially.

Current Density. Single cell tests were run at various current densities to evaluate the performance of the systems. Typical voltage versus time curves at each current density are given in Figure 14. As can be seen at very low current density (20 mA/cm²), life as long as 100 minutes was observed. Even at the designed current density of 90 mA/cm², over 35 minutes' life was attained.

Figure 15 shows the energy density for the Li-Al/FeS₂ system at various current densities compared with that of Ca/CaCrO₄, and Figure 16 shows the variation of cell life to 75% peak voltage with current density for the two systems. From the test results, it is apparent that Li-Al/FeS₂ system promises to substantially extend the present domain of thermal batteries. The highest energy density of 264.7 was obtained at 150 mA/cm²; however, at 90 and 50 mA/cm², the energy density was not too much different.

This data was collected for cells of constant thickness using an 81 mm depolarizer layer. By increasing the thickness of the depolarizer layer and optimizing the composition, this performance could be improved considerably.

TABLE 5

EFFECT OF VARIOUS TREATMENTS OF FeS_2 CELLS ON TRANSIENT PEAK

TREATMENT TO FeS_2	PEAK VOLTAGE	LIFE TO 80% P.V.	LIFE TO 75% P.V.
NONE	2.05	1075	1861
PRESHORTING CELL FOR 10 SECONDS	1.72	2058	2160
PREFUSION OF CELLS FOR 45 SECONDS	1.75	2159	2255
ADDITION OF Li-Al (0.5%)	1.73	1447	1531
ADDITION OF K_2CrO_4 (2.0%)	1.69	1550	1647
ADDITION OF CuCl_2	2.17	43	51

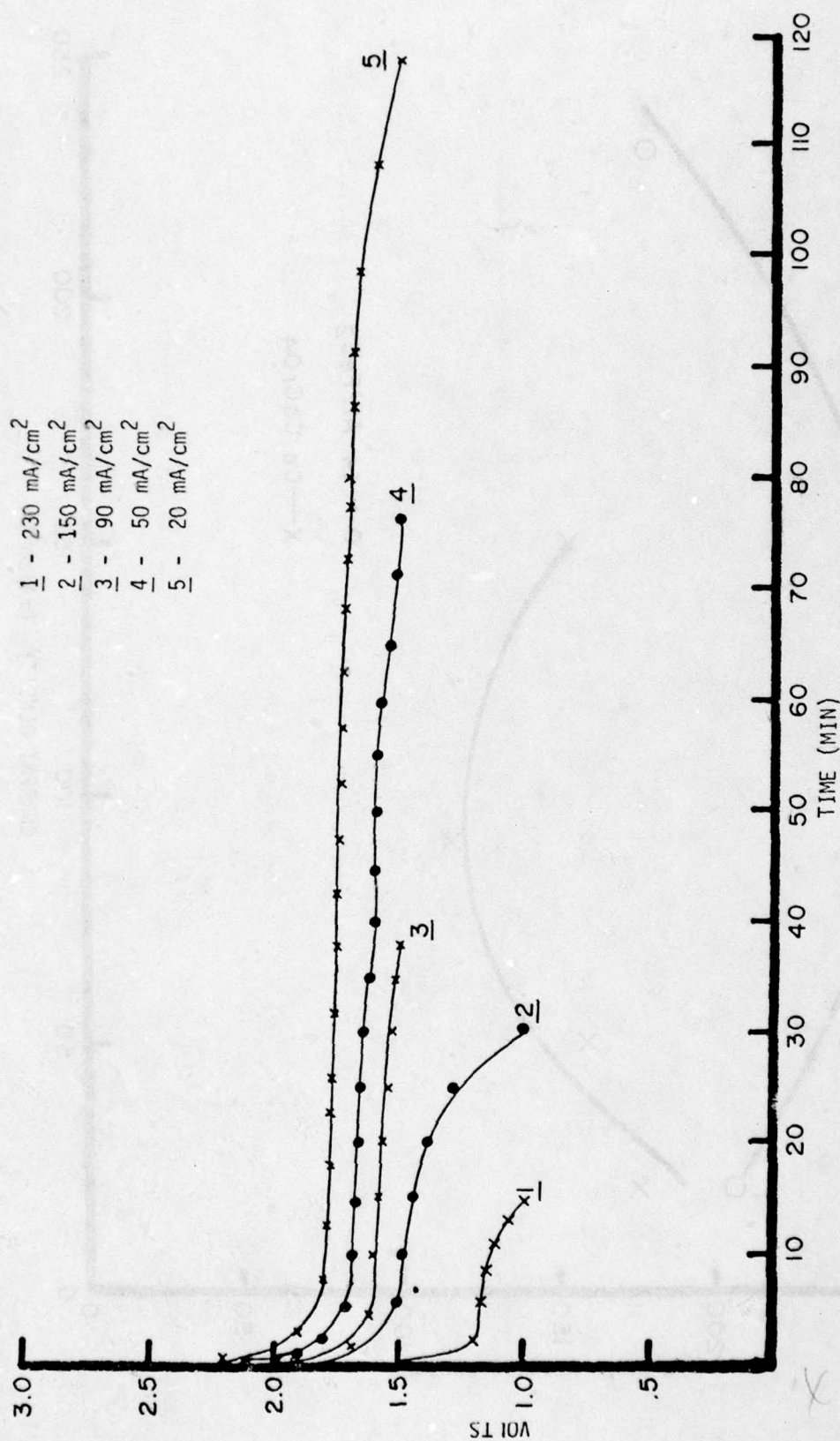


Figure 14. Typical Voltage Vs. Time Curves at Different Current Densities in Single Cell Tests

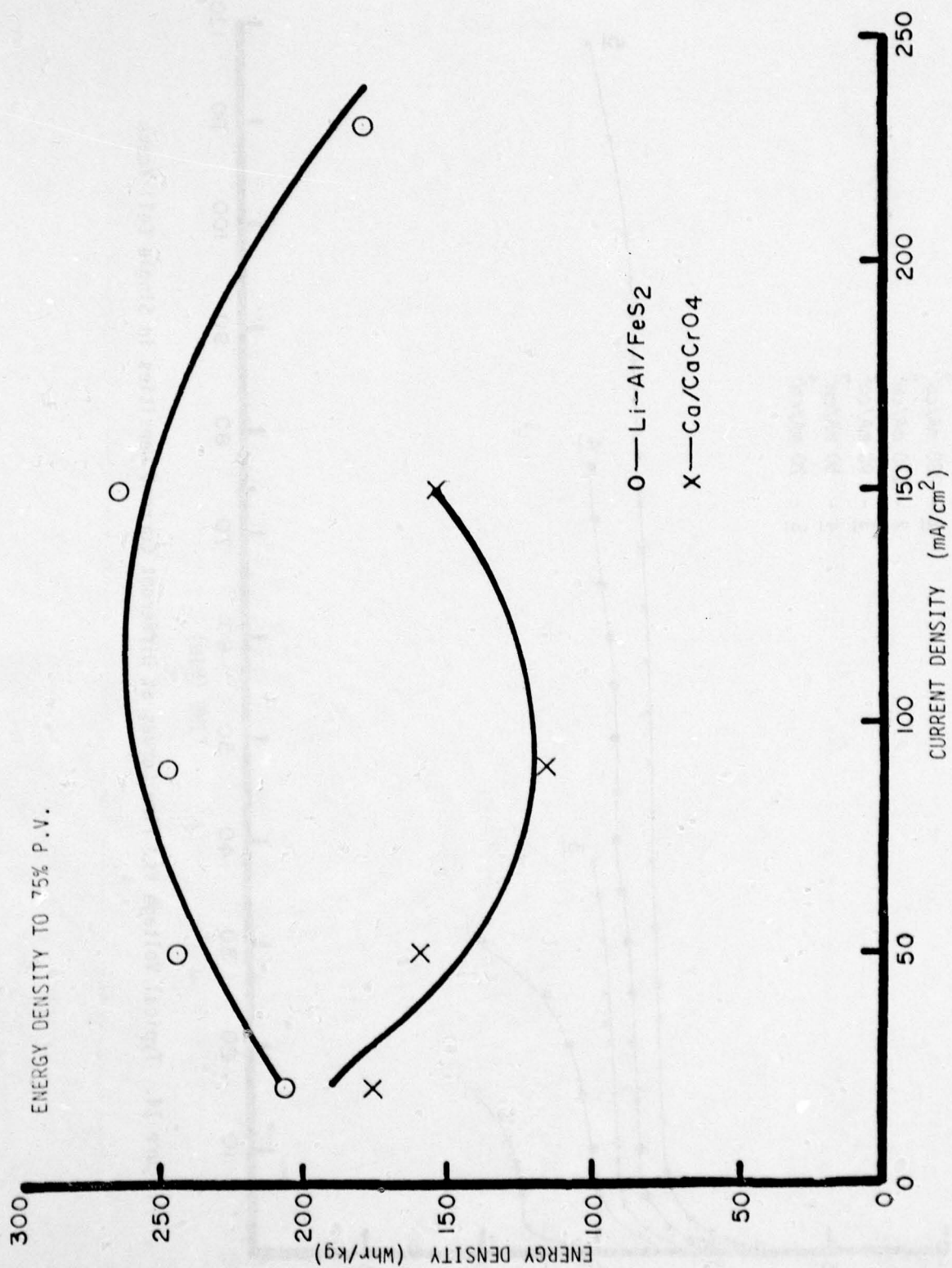


Figure 15. Comparison of Energy Density Vs. Current Density for Li-Al/FeS₂ and Ca/CaCrO₄ Systems in S.C.T.

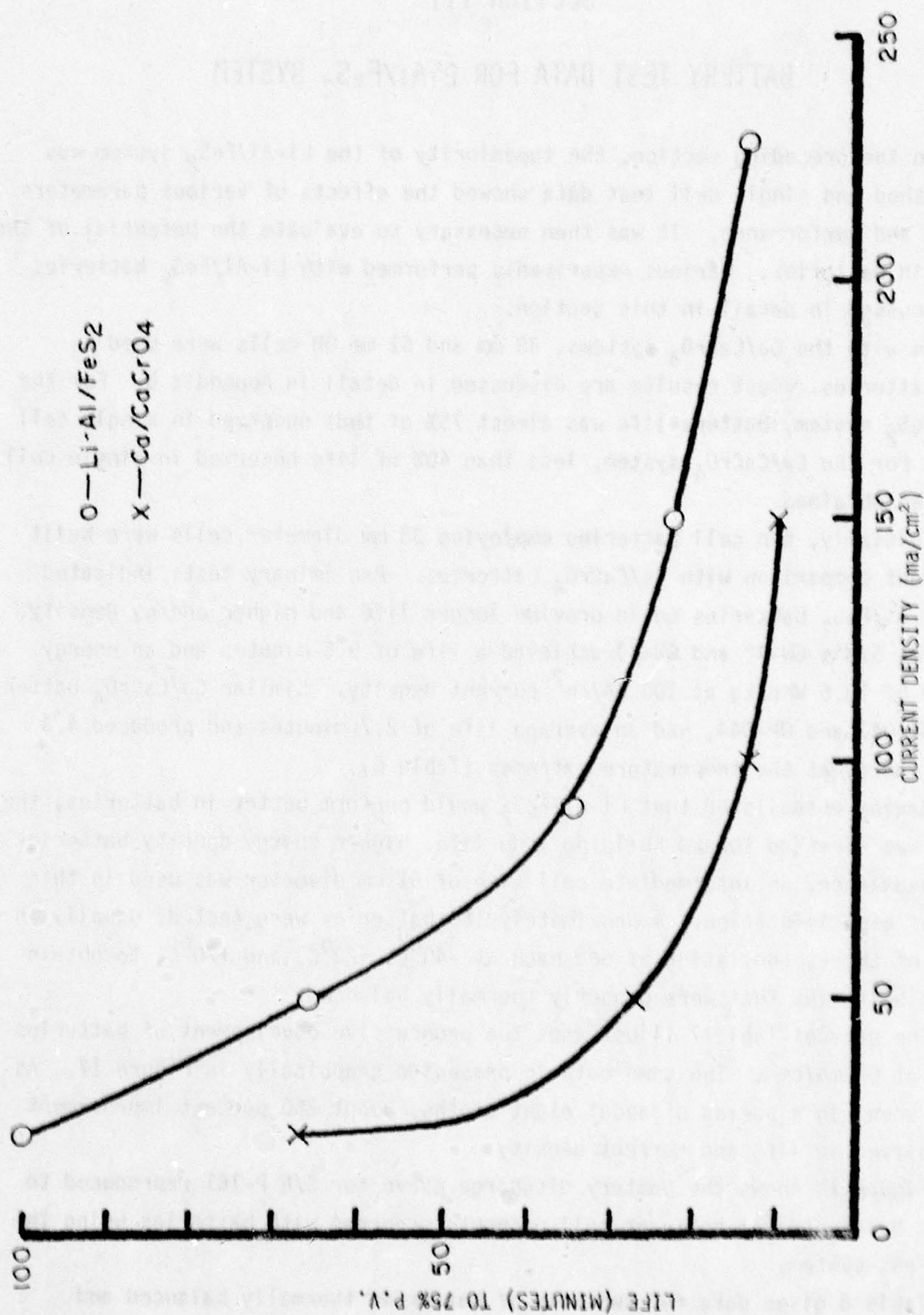


Figure 16. Comparison of Life Vs. Current Density for the Two Systems in Single Cell Tests

SECTION III

BATTERY TEST DATA FOR LiAl/FeS_2 SYSTEM

In the preceding section, the superiority of the Li-Al/FeS_2 system was established and single cell test data showed the effects of various parameters on life and performance. It was then necessary to evaluate the potential of the system in batteries. Various experiments performed with Li-Al/FeS_2 batteries are discussed in detail in this section.

As with the Ca/CaCrO_4 systems, 38 mm and 61 mm OD cells were used to build batteries. Test results are discussed in detail in Appendix D. For the Li-Al/FeS_2 system, battery life was almost 75% of that observed in single cell tests. For the Ca/CaCrO_4 system, less than 40% of life observed in single cell tests was obtained.

Initially, ten cell batteries employing 38 mm diameter cells were built for direct comparison with Ca/CaCrO_4 batteries. Preliminary tests indicated that Li-Al/FeS_2 batteries could provide longer life and higher energy density. Batteries S/N's GW-42 and GW-43 achieved a life of 9.5 minutes and an energy density of 10.6 Whr/kg at 100 mA/cm^2 current density. Similar Ca/CaCrO_4 batteries, S/N's WP-043 and WP-044, had an average life of 2.7 minutes and produced 4.3 Whr/kg energy at the temperature extremes (Table 6).

Having established that Li-Al/FeS_2 would perform better in batteries, the effort was directed toward building long life, higher energy density batteries. For convenience, an intermediate cell size of 61 mm diameter was used in this phase of experimentation. Approximately 160 batteries were tested, usually in groups of three, consisting of one each at -40°C , $+23^\circ\text{C}$, and $+70^\circ\text{C}$, to obtain data on batteries that were properly thermally balanced.

The data of Table 7 illustrates the progressive development of batteries tested at 90 mA/cm^2 . The same data is presented graphically in Figure 17. As can be seen, in a period of about eight months, about 250 percent improvement was achieved in life and current density.

Figure 18 shows the battery discharge curve for S/N P-161 reproduced to scale. No electrical noise or cell dropouts occurred with batteries using the Li-Al/FeS_2 system.

Table 8 gives data for two sets of batteries thermally balanced and tested at 90 mA/cm^2 . Observe that life of over 15 minutes is achieved throughout

TABLE 6

COMPARISON OF BATTERY PERFORMANCE FOR
Ca/CaCrO₄ SYSTEM AND Li-Al/FeS₂ SYSTEM

BATTERY S/N	TEMP.	PEAK VOLTAGE	LIFE TO 75% P.V.	ENERGY DENSITY	REMARKS
	(°C)	(Volts)	(sec)	(Whr/kg)	
WP-043	-40	25.7	161	4.3	Ca/CaCrO ₄ System
WP-044	+70	25.0	164	4.1	Ca/CaCrO ₄ System
GW-42	+70	20.8	572	10.6	Li-Al/FeS ₂ System
GW-43	-40	21.2	413	8.0	Li-Al/FeS ₂ System

38 mm OD cells
No. of cells = 10
Current density = 90 mA/cm²

TABLE 7

PROGRESSIVE DEVELOPMENT OF BATTERY PERFORMANCE
AT 90 mA/cm² CURRENT DENSITY

BATTERY S/N	TEMP.	PEAK VOLTAGE	LIFE TO 75% P.V.	LIFE TO 15V	REMARKS
	(°C)	(Volts)	(sec)	(sec)	
P-31	-40	21.0	420	458	
P-36	+23	21.6	473	617	Change in battery design
P-41	+70	20.5	660	690	Change in thermal balance
P-63	+70	21.2	878	1089	Increased insulation
P-111	+23	20.2	1001	1013	Change of E/D ratio
P-125	+23	20.4	1348	1450	Change of composition
P-131	+23	20.2	1344	1380	Change of composition
P-161	+23	20.8	1411	1540	Change of E/D ratio

System: Li-Al/LiCl-KCl/FeS₂

Ten 61 mm OD cells per stack

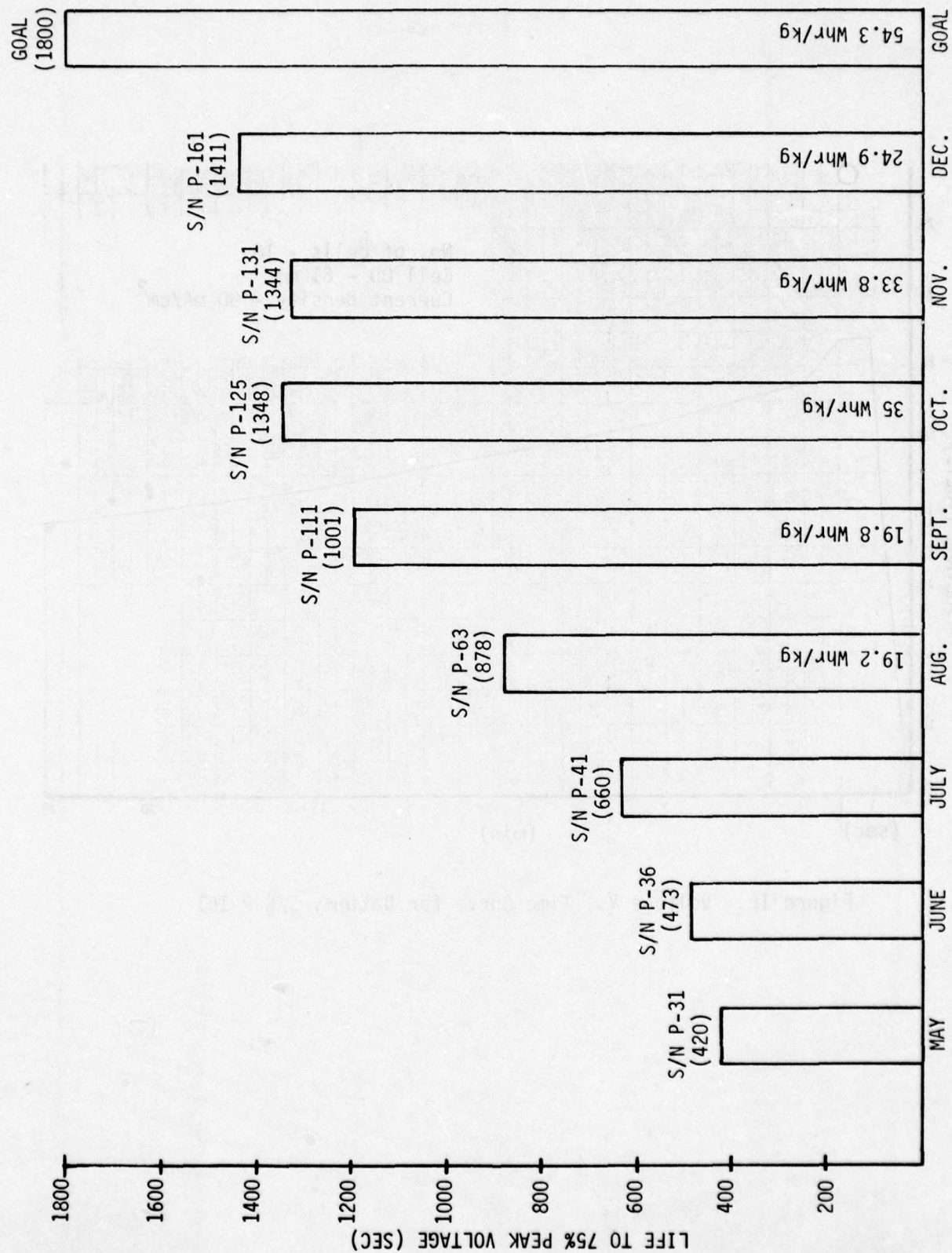


Figure 17. Progress Chart for 10 Cell/Stack Batteries for the System Li-Al/FeS₂

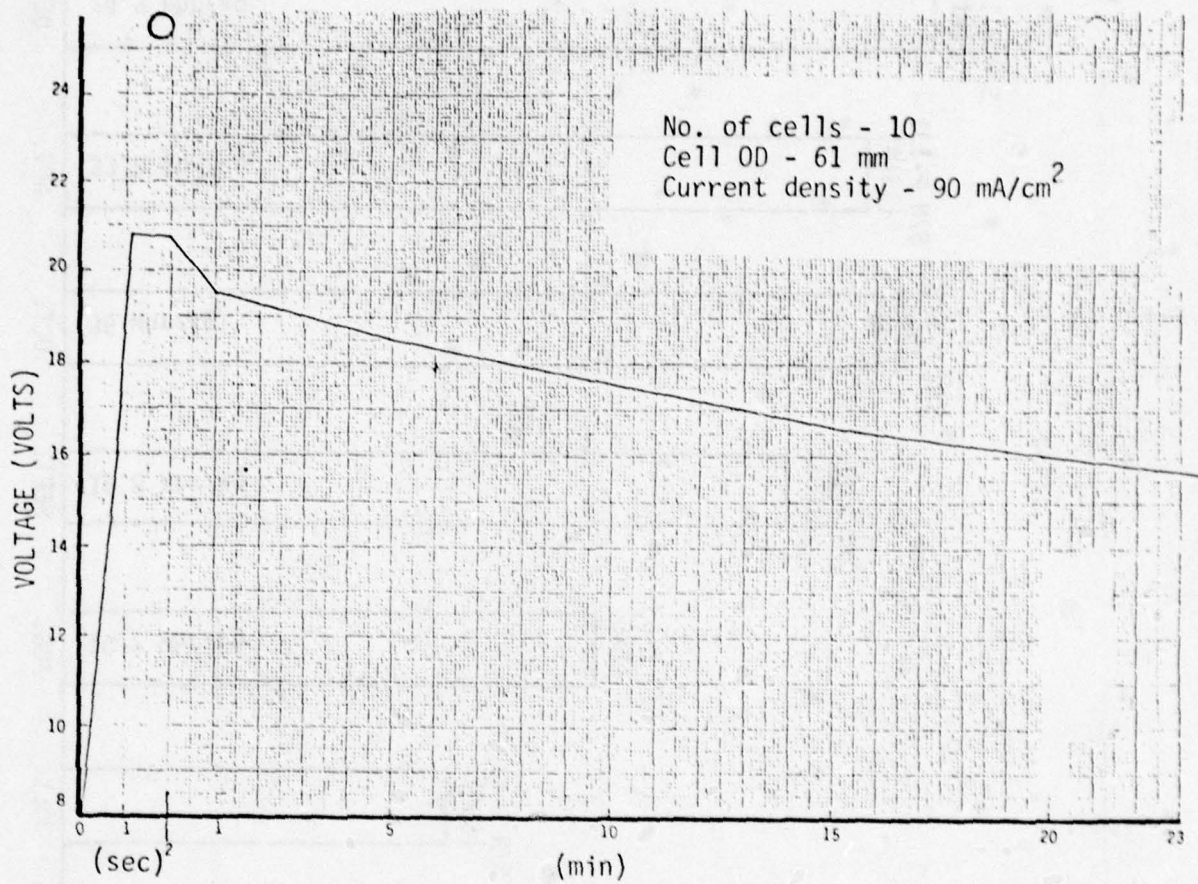


Figure 18. Voltage Vs. Time Curve for Battery S/N P-161

TABLE 8

BATTERY TEST DATA EXHIBITING VARIATION IN PERFORMANCE
AT DIFFERENT AMBIENT TEMPERATURES AT 90 mA/cm² CURRENT DENSITY

BATTERY S/N	TEMP. (°C)	PEAK VOLTAGE (Volts)	START TIME (Sec)	LIFE TO 75% P.V. (Sec)	LIFE TO 15V (Sec)	STACK ENERGY DENSITY	
						Whr/kg	Whr/in ³
P-130	-40	20.0	0.45	854	854	33.8	1.48
P-131	+23	20.2	0.42	1344	1380		
P-132	+70	20.4	0.30	982	1018		
P-133	-40	20.5	0.49	984	995	33.6	1.47
P-134	+23	20.7	0.44	1252	1336		
P-135	+70	21.2	0.46	960	1222		

the ambient temperature range and that start times for these batteries are less than 0.5 seconds.

Batteries were tested at current densities up to 840 mA/cm^2 in order to evaluate the performance as a function of current density. Tests were conducted with both cell sizes and it was found that battery performance does not deteriorate with current density nor with size. Table 9 gives the results for batteries using 61 mm cells and Table 10 gives results for batteries using 38 mm cells. Figure 19 shows the available capacity density (Coulombs/sq.in.) of the batteries plotted against current density. As can be seen, capacity increases with current density for the Li-Al/FeS₂ system and the energy density increases with current density. This is consistent with the single cell test results.

One 10 cell battery (61 mm OD cells) was also tested with pulses up to 2000 mA/cm^2 applied every 50 seconds. Battery internal resistance was measured at 0.12 ohms (.012 ohms per cell) and was accomplished without loss of total capacity or overall performance. Thus, the great superiority of the Li-Al/FeS₂ system over the Ca/CaCrO₄ system is clearly illustrated.

Since it was estimated that the final battery would require three stacks in parallel at 90 mA/cm^2 , several batteries were tested with two or three stacks in parallel. It was found that there was no loss in life, but that the two stack battery was less efficient on the basis of energy density than the three stack battery. The results are given in Table 11.

The resulting effect of using buffer pellets was about 20% improvement in battery performance. Therefore, they were incorporated in all subsequent experimental batteries. Test results are given in Table 12. The units with buffer pellets were, in general, not perfectly thermally balanced for high and low temperature operation, but this is readily correctable.

Because all the above batteries were tested under static conditions, it was decided to evaluate some under vibration, shock, and acceleration. Again, the Li-Al/FeS₂ proved superior to the Ca/CaCrO₄ system. The results and conditions for these tests in which 38 mm cells were used are shown in Table 13.

Finally, several batteries of improved design were tested to study performance at current densities from 50 to 150 mA/cm^2 . The results are given in Table 14. From the results it can be observed that at 90 mA/cm^2 the longest life of 23.5 minutes was obtained by battery S/N P-161. It is thus concluded that a battery using three stacks in parallel is capable of delivering 30

TABLE 9

TEN CELL BATTERY (61 mm OD CELLS) TEST RESULTS
AT DIFFERENT CURRENT DENSITIES

BATTERY S/N	TEMP.	CURRENT DENSITY	PEAK VOLTAGE	START TIME	LIFE TO 75% P.V.	STACK ENERGY DENSITY
	(°C)	(ma/cm ²)	(Volts)	(sec)	(sec)	(Whr/kg)
P-64	+23	90	21.1	0.42	844	20.5
P-80	+23	200	20.0	0.43	371	25.6
P-81	+23	360	16.9	0.51	198	20.2
P-78	+23	500	18.3	0.63	188	27.1
P-79	+23	635	17.0	0.54	155	27.7
P-77	+23	790	16.9	0.66	120	25.1

SYSTEM: Li-Al/LiCl-KCl/FeS₂

TABLE 10

TEN CELL BATTERY (38 mm OD CELLS) TEST RESULTS
AT DIFFERENT CURRENT DENSITIES

BATTERY S/N	TEMP.	CURRENT DENSITY	PEAK VOLTAGE	START TIME	LIFE TO 75% P.V.	STACK ENERGY DENSITY
	(°C)	(ma/cm ²)	(Volts)	(sec)	(sec)	(Whr/kg)
P-142	+23	95	21.2	0.53	722	22.4
P-143	+23	210	20.7	0.62	340	23.1
P-144	+23	420	19.9	0.63	234	30.3
P-145	+23	540	19.6	0.67	188	30.6
P-149	+23	720	19.3	0.63	145	30.8
P-151	+23	840	18.2	0.66	114	26.8

SYSTEM: Li-Al/LiCl-KCl/FeS₂

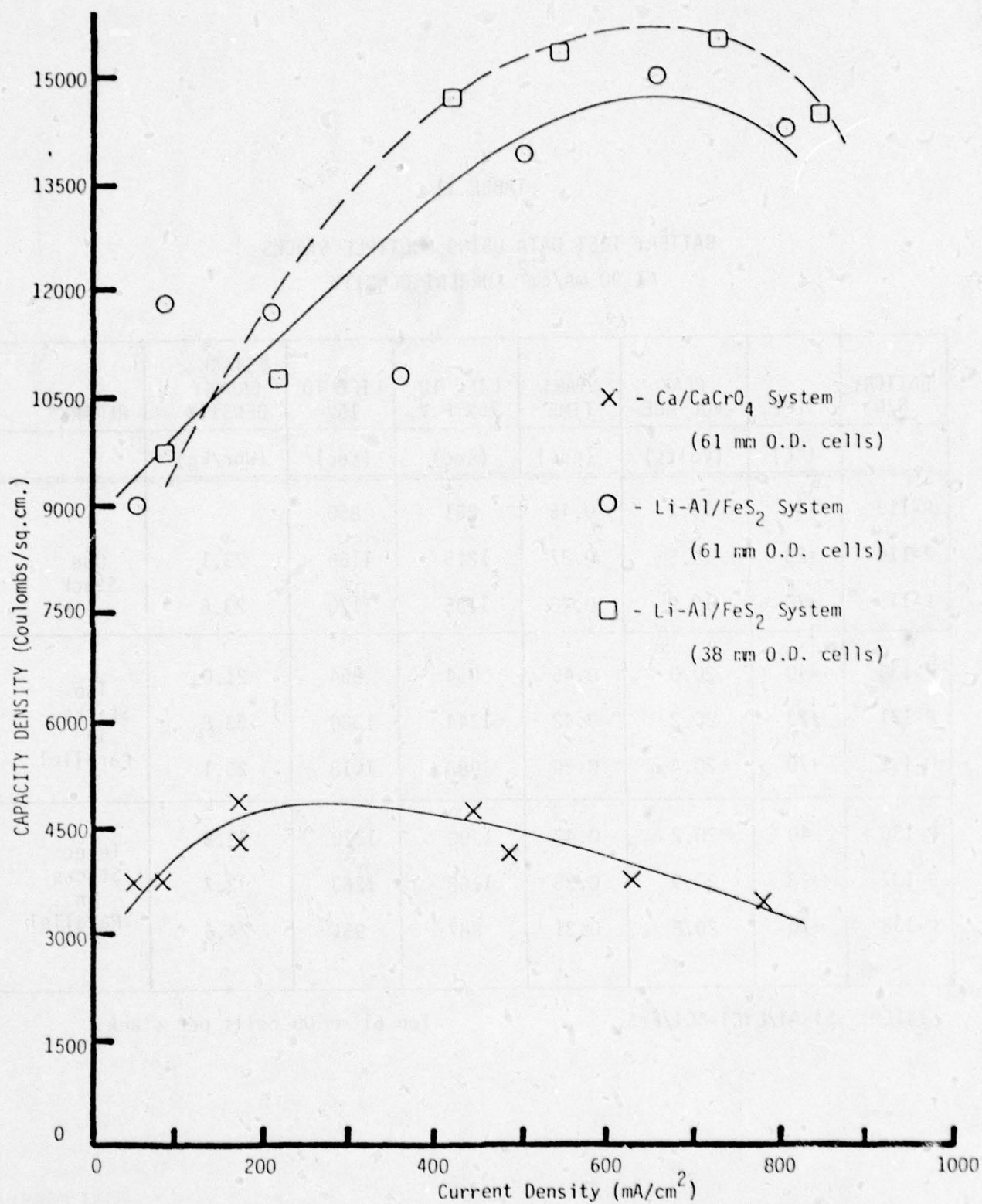


Figure 19. Effect of Current Density on Capacity Density in Battery Tests

TABLE 11

BATTERY TEST DATA USING MULTIPLE STACKS
AT 90 mA/cm² CURRENT DENSITY

BATTERY S/N	TEMP.	PEAK VOLTAGE	START TIME	LIFE TO 75% P.V.	LIFE TO 15V	STACK ENERGY DENSITY	REMARKS
	(°C)	(Volts)	(sec)	(sec)	(sec)	(Whr/kg)	
P-113	-40	19.2	0.45	881	850		One Stack
P-114	+23	19.5	0.37	1215	1166	23.1	
P-115	+70	19.9	0.28	1195	1170	23.6	
P-130	-40	20.0	0.45	854	854	21.0	Two Stacks in Parallel
P-131	+23	20.2	0.42	1344	1380	33.8	
P-132	+70	20.4	0.30	982	1018	25.1	
P-136	-40	20.2	0.42	1290	1320	33.8	Three Stacks in Parallel
P-137	+23	20.9	0.38	1168	1263	32.7	
P-138	+70	20.8	0.31	887	951	24.6	

SYSTEM: Li-Al/LiCl-KCl/FeS₂

Ten 61 mm OD cells per stack

TABLE 12

EFFECT OF USING BUFFER PELLETS IN THERMAL BATTERIES
AT 90 mA/cm² CURRENT DENSITY

BATTERY S/N	TEMP.	PEAK VOLTAGE	LIFE TO 75% P.V.	LIFE TO 15V	STACK ENERGY DENSITY	REMARKS
	(°C)	(Volts)	(sec)	(sec)	(Whr/kg)	
P-110	-40	20.0	723	724	-	No buffer pellets
P-111	+23	20.2	1001	1013	19.8	No buffer pellets
P-112	+70	20.2	984	1009	-	No buffer pellets
P-113	-40	19.2	881	850		Buffer pellets
P-114	+23	19.5	1215	1161	23.1	Buffer pellets
P-115	+70	19.9	1195	1170	23.6	Buffer pellets

System: Li-Al/LiCl-KCl/FeS₂

Ten 61 mm OD cells

TABLE 13

THERMAL BATTERY TEST DATA UNDER DYNAMIC CONDITIONS
38 mm CELL DIAMETER

SERIAL NUMBER	CURRENT DENSITY (mA/cm ²)	PEAK VOLTAGE (Volts)	RISE TIME (msec)	LIFE TO 75% PEAK VOLTAGE (sec)
P-146	230	20.04	580	302
	(30 G shock for 50 msec every 45 sec: Per MIL-STD-810C, Method 516.2)			
P-147	230	20.00	610	301
	(30 G Longitudinal acceleration; continuous: Per MIL-STD-810C, Method 513.2)			
P-148	230	20.80	120	316
	(Longitudinal Vibration 5 Hz-500 Hz for 5 minutes at 10 G: per MIL-STD-810C, Method 514.2, Procedure I, Part 2 Curve D of 514.2.2, Table 514.2-II)			
P-150	135	20.10	640	520
	Lateral acceleration: t(sec) G 0 - 60 5 60 - 120 10 120 - 180 20 180 - 210 30 (increase of 10 G every 30 seconds) 410 - 520 105 G			

BATTERY CHARACTERISTICS: Number of cells 10
 Cell area 1.74 sq. in.
 Battery diameter 2.24"
 Battery height 3.45"
 Battery weight 420 grams

TEST CONDITION: Dynamic (As specified)

TEST TEMPERATURE: +23°C

SYSTEM: Li-Al/LiCl-KCl/FeS₂

TABLE 14

BATTERY TEST RESULTS AT VARIOUS CURRENT DENSITIES
TEN 61 mm OD CELLS/STACK

BATTERY S/N	CURRENT DENSITY	PEAK VOLTAGE	LIFE TO 75% P.V.	LIFE TO 15V	STACK ENERGY DENSITY	REMARKS
	(mA/cm ²)	(Volts)	(sec)	(sec)	(Whr/kg)	
P-159*	90	21.0	1177	1305	24.4	Increased anode
P-161*	90	20.8	1411	1540	24.9	Increased anode and cathode
P-163*	150	21.0	797	1082	21.2	Increased cathode
P-154	150	21.0	675	830	38.4	Standard cells, 2 stacks in parallel.
P-155	135	21.0	735	871	37.3	
P-156	50	21.9	1191	1517	24.6	

*Single stack batteries

SYSTEM: Li-Al/LiCl-KCl/FeS₂

amperes for at least 23.5 minutes (78% of desired life). However, if the battery were designed for operation at 150 mA/cm^2 , only two stacks would be required and its total volume would be significantly reduced. Based on the longest life obtained at 150 mA/cm^2 (S/N P-163, life to 75% peak voltage is 13.3 minutes), the final battery is projected to operate longer than 15 minutes at -40°C and $+70^\circ\text{C}$ and over 18 minutes at $+23^\circ\text{C}$. The final volume is also expected to be increased 40% from the goal value of 144 cubic inches.

TEST NO.	TEMPERATURE (°C)	TEST TIME (min)	PEAK VOLTAGE (V)	75% VOLTAGE (V)	75% TIME (min)	75% LIFE (min)
1	-40	10	1.15	1.05	10	10
2	-40	15	1.15	1.05	15	15
3	-40	20	1.15	1.05	20	20
4	-40	25	1.15	1.05	25	25
5	-40	30	1.15	1.05	30	30
6	-40	35	1.15	1.05	35	35
7	-40	40	1.15	1.05	40	40
8	-40	45	1.15	1.05	45	45
9	-40	50	1.15	1.05	50	50
10	-40	55	1.15	1.05	55	55
11	-40	60	1.15	1.05	60	60
12	-40	65	1.15	1.05	65	65
13	-40	70	1.15	1.05	70	70
14	-40	75	1.15	1.05	75	75
15	-40	80	1.15	1.05	80	80
16	-40	85	1.15	1.05	85	85
17	-40	90	1.15	1.05	90	90
18	-40	95	1.15	1.05	95	95
19	-40	100	1.15	1.05	100	100
20	-40	105	1.15	1.05	105	105
21	-40	110	1.15	1.05	110	110
22	-40	115	1.15	1.05	115	115
23	-40	120	1.15	1.05	120	120
24	-40	125	1.15	1.05	125	125
25	-40	130	1.15	1.05	130	130
26	-40	135	1.15	1.05	135	135
27	-40	140	1.15	1.05	140	140
28	-40	145	1.15	1.05	145	145
29	-40	150	1.15	1.05	150	150
30	-40	155	1.15	1.05	155	155
31	-40	160	1.15	1.05	160	160
32	-40	165	1.15	1.05	165	165
33	-40	170	1.15	1.05	170	170
34	-40	175	1.15	1.05	175	175
35	-40	180	1.15	1.05	180	180
36	-40	185	1.15	1.05	185	185
37	-40	190	1.15	1.05	190	190
38	-40	195	1.15	1.05	195	195
39	-40	200	1.15	1.05	200	200
40	-40	205	1.15	1.05	205	205
41	-40	210	1.15	1.05	210	210
42	-40	215	1.15	1.05	215	215
43	-40	220	1.15	1.05	220	220
44	-40	225	1.15	1.05	225	225
45	-40	230	1.15	1.05	230	230
46	-40	235	1.15	1.05	235	235
47	-40	240	1.15	1.05	240	240
48	-40	245	1.15	1.05	245	245
49	-40	250	1.15	1.05	250	250
50	-40	255	1.15	1.05	255	255
51	-40	260	1.15	1.05	260	260
52	-40	265	1.15	1.05	265	265
53	-40	270	1.15	1.05	270	270
54	-40	275	1.15	1.05	275	275
55	-40	280	1.15	1.05	280	280
56	-40	285	1.15	1.05	285	285
57	-40	290	1.15	1.05	290	290
58	-40	295	1.15	1.05	295	295
59	-40	300	1.15	1.05	300	300
60	-40	305	1.15	1.05	305	305
61	-40	310	1.15	1.05	310	310
62	-40	315	1.15	1.05	315	315
63	-40	320	1.15	1.05	320	320
64	-40	325	1.15	1.05	325	325
65	-40	330	1.15	1.05	330	330
66	-40	335	1.15	1.05	335	335
67	-40	340	1.15	1.05	340	340
68	-40	345	1.15	1.05	345	345
69	-40	350	1.15	1.05	350	350
70	-40	355	1.15	1.05	355	355
71	-40	360	1.15	1.05	360	360
72	-40	365	1.15	1.05	365	365
73	-40	370	1.15	1.05	370	370
74	-40	375	1.15	1.05	375	375
75	-40	380	1.15	1.05	380	380
76	-40	385	1.15	1.05	385	385
77	-40	390	1.15	1.05	390	390
78	-40	395	1.15	1.05	395	395
79	-40	400	1.15	1.05	400	400
80	-40	405	1.15	1.05	405	405
81	-40	410	1.15	1.05	410	410
82	-40	415	1.15	1.05	415	415
83	-40	420	1.15	1.05	420	420
84	-40	425	1.15	1.05	425	425
85	-40	430	1.15	1.05	430	430
86	-40	435	1.15	1.05	435	435
87	-40	440	1.15	1.05	440	440
88	-40	445	1.15	1.05	445	445
89	-40	450	1.15	1.05	450	450
90	-40	455	1.15	1.05	455	455
91	-40	460	1.15	1.05	460	460
92	-40	465	1.15	1.05	465	465
93	-40	470	1.15	1.05	470	470
94	-40	475	1.15	1.05	475	475
95	-40	480	1.15	1.05	480	480
96	-40	485	1.15	1.05	485	485
97	-40	490	1.15	1.05	490	490
98	-40	495	1.15	1.05	495	495
99	-40	500	1.15	1.05	500	500
100	-40	505	1.15	1.05	505	505

SECTION IV

CONCLUSION

In June 1976, KDI SCORE was awarded a program to develop a 28 volt, 30 ampere, 30 minute thermal battery in a 144 cubic inch envelope and weighing 17 pounds. This was considered a very ambitious goal requiring a significant advance in the state-of-the-art of the existing systems.

Preliminary calculations suggested that the Ca/CaCrO_4 system utilizing three paralleled stacks of 12 cells each, operating at $90 \text{ mA}/\text{cm}^2$ over a 120 mm OD cell, could provide the necessary current. The problem was to determine the optimum conditions for the system or to find a superior alternative system.

An exhaustive study of the $\text{Ca}/\text{LiCl-KCl}/\text{CaCrO}_4$ system was conducted and, as a result, sufficient test data are presented in Appendix D for determining composition, thickness, density, and configuration of the required pellet. The study also included investigation of the physical, chemical, and thermal properties of the components of the system. Based on the battery results, it can be observed that at $90 \text{ mA}/\text{cm}^2$, the longest life attained was about 5 minutes and that approximately 10 minutes could be projected. Longer life is, however, possible at a current density of $15 \text{ mA}/\text{cm}^2$. At $50 \text{ mA}/\text{cm}^2$, longest life attained in a battery was about 10 minutes. However, one might obtain 15 minutes' life under special conditions. Thus, the best battery performance projected with the Ca/CaCrO_4 system is 28 volts, 15 amperes, for 15 minutes, operating at $50 \text{ mA}/\text{cm}^2$.

This led to the investigation of a number of new electrochemical systems (Section II), as a result of which $\text{Li-Al}/\text{FeS}_2$ was found to operate in single cell tests at $90 \text{ mA}/\text{cm}^2$ for over 35 minutes while providing an energy density of 248.9 Whr/kg.

In a rather limited time, KDI SCORE advanced from single cell tests to battery development using the $\text{Li-Al}/\text{LiCl-KCl}/\text{FeS}_2$ system and successfully tested batteries over the temperature range of -40°C to $+70^\circ\text{C}$. Life of 24 minutes at $90 \text{ mA}/\text{cm}^2$ (80% of the projected goal) and energy density of 38.4 Whr/kg (78% of the projected goal) were achieved.

Following are the advantages of the $\text{Li-Al}/\text{LiCl-KCl}/\text{FeS}_2$ system over the $\text{Ca}/\text{LiCl-KCl}/\text{CaCrO}_4$ system:

- 1) It has an anode which is solid at operating temperature, thereby precluding failures attributable to the liquid metal alloy.
- 2) It operates over a 140 to 150°C temperature range without significant loss of performance.
- 3) It exhibits very low electrical noise.
- 4) It provides three to four times greater energy densities up to 1000 mA/cm².
- 5) Batteries using it exhibit very predictable performance. Up to 75% of the life observed in single cell tests has been obtained in the batteries, whereas less than 50% life was possible with the Ca/CaCrO₄ system.
- 6) It is capable of providing longer battery lives (over 20 minutes) at higher current densities.
- 7) Batteries using it will be less costly and more reliable.
- 8) It can withstand more severe dynamic conditions.
- 9) It exhibits very low internal resistance and is therefore capable of sustaining very high current pulses (up to 2000 mA/cm²).

The relatively low cell potential of the Li-Al/LiCl-KCl/FeS₂ system is likely to restrict its use in low current, short life applications in which battery length is more critical than total volume since more cells are required for a given battery voltage than with Ca/LiCl-KCl/CaCrO₄. However, the difference in the cell potentials of the two systems decreases with increasing current density because of the much lower internal resistance of the Li-Al/LiCl-KCl/FeS₂ cell. Therefore, at high current densities there is little difference in battery lengths required for the two systems and the Li-Al/LiCl-KCl/FeS₂ battery will be smaller in diameter. In many cases a single Li-Al/LiCl-KCl/CaCrO₄ stack may be used instead of parallel Ca/LiCl-KCl/CaCrO₄ stacks, thus providing a battery of reduced length.

Table 15 shows some of the battery results which are discussed in detail in Section III. A 30 ampere battery operating at 90 mA/cm² for over 20 minutes over the entire temperature range is believed feasible. The volume of such a battery would exceed the desired goal. However, at 150 mA/cm², only two stacks in parallel are required and over 15 minutes life could be obtained. The battery volume goal would be exceeded by about 35%.

Following are the areas recommended for further investigation for achievement of the final goal:

- 1) Elimination of the initial transient voltage peak to provide a linear discharge curve, in order to increase life.
- 2) Use of other anodes to obtain higher peak voltages.
- 3) Use of all Li^+ containing electrolytes as against LiCl-KCl .
- 4) Better definition of the reaction mechanism in the battery at different current densities.

TABLE 18
COMPARISON OF TEST RESULTS DATA WITH DATA

DRY-CELL CURRENT (mA)	DRY-CELL VOLTAGE (V)	DRY-CELL CAPACITY (mAh)	DRY-CELL INTERNAL RESISTANCE (Ω)	DRY-CELL SELF-DISCHARGE (%/yr)	DRY-CELL LIFE (hrs)
0.10	1.45	1.5	1.5	0.5	100
0.15	1.40	1.5	1.5	0.5	100
0.20	1.35	1.5	1.5	0.5	100
0.25	1.30	1.5	1.5	0.5	100

TABLE 15

COMPARISON OF BEST BATTERY DATA WITH GOAL

BATTERY S/N	CURRENT DENSITY	PEAK VOLTAGE	LIFE TO 75% P.V.	LIFE TO 15V	STACK ENERGY DENSITY
	(mA/cm ²)	(Volts)	(min)	(min)	(Whr/kg)
GOAL	-	32	30	-	54.0
P-131	90	30.2	22.3	24.0	33.8
P-161	90	20.8	23.5	25.6	24.9
P-163	150	21.0	13.3	18.0	21.2

System: Li-Al/LiCl-KCl/FeS₂

APPENDIX A

TECHNICAL PLAN

A comprehensive literature survey was conducted at the start of the program. It indicated that a wide variety of materials was used in many different ways; e.g., insulation, composition of powder mixes, electrolytes, and depolarizers. Information previously considered to be of little scientific value was found to be highly significant in conjunction with current technology, materials, processing, and production methods.

To supplement the study of the chemical components of the electrochemical system, the following modes of testing were used.

Laboratory Testing (Physical and Chemical Analysis). Powder mixes were analyzed qualitatively and quantitatively for composition using volumetric titrations and atomic absorption, respectively. A Jarrell-Ash spectrophotometer, JA 82-720, was used. Particle size was measured using a Fisher subsieve sizer and Fisher sieves to study the relationship between particle size and battery performance.

Thermal Analysis. The chemical mixes and their components were analyzed for their thermal behaviors using a differential scanning calorimeter, Perkin-Elmer DSC-2. The purpose of this technique is to study the thermal requirements of the chemical mixes and the physicochemical changes taking place during their heating and cooling. The calorific values of the pyrotechnic mixes were evaluated using a Parr oxygen bomb calorimeter.

Single Cell Testing. Each cell was constructed by placing a pellet between the anode and the cathode current collector. The systems were evaluated by means of an instrumented single cell tester using heated boron nitride platens for cell activation. The tester was similar to that described in Sandia Laboratories Report SLA73-0896. Platen temperatures were controlled to within $\pm 10^{\circ}\text{C}$.

A test cell was placed between the heated platens at constant temperature and pressure, and leads from the anode and cathode collectors were then connected to the desired load. Data was recorded for voltage on load, current, pressure, and temperature, using a Hewlett-Packard recording system (HP Model 7418A with HP8803A amplifiers). Life was measured at the time required for the load voltage to drop by 25% of its peak value. Temperature

and pressure for each system were optimized and the data reported herein are for current densities of 50 mA/cm^2 , 90 mA/cm^2 , and 150 mA/cm^2 .

Small Battery Testing. The systems found most promising in single cell tests were further evaluated in ten 10 cell batteries. Two cell sizes (38 mm and 61 mm) were evaluated. These batteries were tested over the temperature range of -40°C to $+71^\circ\text{C}$. Life was measured for specific voltage drops at current densities corresponding to those of the single cell tests. This was done to provide comparative data for single cells and batteries.

Final Battery Testing. Feasibility studies were conducted to establish a preliminary baseline design. Any systems which exhibited the required performance in both single cell and small battery tests, were evaluated in a final battery configuration using 110 mm OD cells.

In order to systematically approach the problems involved and to establish relationships between test results and the required battery design, a prioritized list of areas of investigation was developed as follows:

- Physicochemical Studies
- Electrochemical Studies
- Electrical and Thermal Techniques
- Fusible Heat Reservoirs
- Pyrotechnic Studies
- Advanced Insulation
- Battery Geometry
- Case Material
- New Electrochemical Studies

Physicochemical Studies. This area was divided into two categories:

- 1) Chemical studies
- 2) Thermal Studies

The individual chemicals, their mixtures, and other battery components were evaluated for their chemical and thermal characteristics. This helped in standardization of materials and establishment of proper quality control procedures. The studies made under this title are further discussed in detail in Appendix C.

Electrochemical studies. The major portion of the program was concentrated in this area. Most of the work was with the $\text{Ca/LiCl-KCl/CaCrO}_4$

system. Twenty-five percent of the effort was devoted to new electrochemical systems. These studies are discussed in detail in Appendix D of this report.

Electrical and Thermal Techniques. Feasibility studies were made of these techniques and these techniques are discussed in Appendix E of this report.

Fusible Heat Reservoirs. Eutectic buffer pellets of $\text{Li}_2\text{SO}_4\text{-NaCl}$ and various non-eutectic compositions were evaluated along with other heat sinks. Ultimately, a heat reservoir was selected which best assured proper battery performance.

Pyrotechnic Studies. A comparison of the zirconium-barium chromate heat paper system with the iron-potassium perchlorate heat pellet system was conducted.

Advanced Insulation. A survey of most of the appropriate high temperature insulating materials was conducted and the Min-K Type TE-1400 produced by Johns Manville was found to be the best candidate. Its thermal conductivity at 1000°F is $0.27 \text{ BTU-in}/^\circ\text{C}/\text{ft}^2/\text{hr}$.

Battery Geometry. A theoretical study for optimizing battery geometry was devised to minimize thermal loss as the limiting factor for battery life. This study was to:

- 1) Minimize battery surface area to volume ratio,
- 2) Maximize active cell surface area, and
- 3) Minimize cell surface area cooled per unit time.

However, the study was not completed due to lack of funds and time.

Case Material. An investigation of aluminum, titanium, and other metals and alloys for impact on weight and energy density was planned; but, due to lack of funds and time, these studies were dropped.

New Electrochemical Studies. In addition to study of the $\text{Ca/KCl-LiCl/CaCrO}_4$ system, about 25% of the time was to be spent in evaluating other electrochemical systems. However, it was determined that the desired goals could not be attained with the Ca/CaCrO_4 system, and more time was spent on other systems.

A study was conducted to evaluate the feasibility of aluminum, lithium, calcium, or their alloys, as the system anode materials:

$\text{Ca, Al, Li, alloys/LiCl-KCl/CaCrO}_4$

A study was also conducted to evaluate the feasibility of replacing calcium chromate with other prospective cathodic materials:

Calcium		Metal Oxides
Aluminum	LiCl-KCl	Metal Sulfides
Lithium		Other Chromates
or Alloys		

APPENDIX B

ELECTROCHEMICAL MIXES

The following tables give the compositions of the powder mixes (and the combinations thereof) used for evaluation in single cell tests and batteries.

The nomenclatures which are used are:

- WPH - Homogeneous Powder Mixes
- WPE - Electrolyte Powder Mixes
- WPD - Depolarizer Powder Mixes
- WPN - New Depolarizer Powder Mixes
- L - Anode Powder Mixes

TABLE B-1

HOMOGENEOUS POWDER MIXES (WPH SERIES)
SINGLE LAYER SYSTEMS

POWDER	%SALT	%CaCrO ₄	%K ₂ CrO ₄	% OTHER	% OTHER	% OTHER	CAB-O-SIL ₆	NOTES
WPH-1	56.00	37.00					7.0	(1)
WPH-2	58.00	32.00					10.0	(2)
WPH-3	55.00	28.80	5.0	3.2 PbCrO ₄			8.0	
WPH-4	52.00	37.00			4.0 Ca(OH) ₂		7.0	
WPH-5	53.00	28.00	4.5	3.0 PbCrO ₄		4.5 CrO ₃	7.0	
WPH-6	52.00	37.00			4.0 Ca(OH) ₂		7.0	(3)
WPH-7	56.40	31.10					12.5	
WPH-8	58.00	35.00					7.0	
WPH-9	59.60	36.40					4.0	
WPH-10	54.0	36.00					10.0	
WPH-11	52.50	35.00					12.5	
WPH-12	55.78	34.22					10.0	
WPH-13	54.23	33.37					12.5	
WPH-14	57.60	38.40					4.0	
WPH-15	55.40	30.60					14.0	
WPH-16	55.91	30.84					13.25	
WPH-17	59.80	33.20					7.0	
WPH-18	61.70	34.30					4.0	

(1) SANDIA Formulation

(2) SCORE Formulation

(3) Ca(OH)₂ fused w/salt

TABLE B-2

ELECTROLYTE MIXES (WPE SERIES)
TWO LAYER SYSTEMS

POWDER	%SALT	%CaCrO ₄	%K ₂ CrO ₄	% OTHER	% OTHER	% OTHER	CAB-0-SIL%	NOTES
WPE-1	76.0	12.0					12.0	(1)
WPE-2	77.0		13.0				10.0	
WPE-3	74.4		15.6				10.0	
WPE-4	72.0		14.5		5.5 Ca(OH) ₂		8.0	
WPE-5	74.4				15.6 Ca(OH) ₂		10.0	
WPE-6	74.4				15.6 Li ₂ CrO ₄		10.0	
WPE-7	70.7		14.8			5 Fe	9.5	
WPE-8	55.1	30.4				5 Fe	9.5	
WPE-9	85.0						15.0	
WPE-10	85.0			15Y ₂ O ₃				
WPE-11	80.0			20Y ₂ O ₃				
WPE-12				9.6 LiF	22.03 LiCl	68.4 LiBr		
WPE-13				43.89 LiOH	56.2 LiCl			
WPE-14				85 WPE-13			15.0	
WPE-15				60 WPE-13	40 Y ₂ O ₃			
WPE-16	49.0			41 LiCl			10.0	
WPE-17				11.5 KCl	43.5 LiOH			
WPE-18				85 WPE-12			15.0	
WPE-19				85 WPE-17			15.0	
WPE-20	60.0				40 Y ₂ O ₃			

(1) SCORE Formulation

TABLE B-3

 DEPOLARIZER MIXES (WPD SERIES)
 TWO LAYER SYSTEMS

POWDER	%SALT	%CaCrO ₄	%K ₂ CrO ₄	% OTHER	% OTHER	% OTHER	CAB-O-SIL%	NOTES
WPD-1	25.0	70.0					5.0	(1)
WPD-2	38.7	50.0	6.5				4.8	
WPD-3	23.5	66.7	7.8				2.0	
WPD-4	22.5	64.5	7.0			5.0 CrO ₃	1.0	
WPD-5	23.5	54.5		20 Li ₂ CrO ₄			2.0	
WPD-6				95 WPD-3	5.0 C (Graphite)			
WPD-7				95 WPD-3	5.0 Cu			
WPD-8				95 WPD-3	5.0 Ni			
WPD-9	23.0	53.0		20 ZnCrO ₄			4.0	
WPD-10	55.1	30.4			5.0 Cu		9.5	
WPD-11	55.1	30.4			5.0 C		9.5	
WPD-12	55.1	30.4			5.0 Ni		9.5	
WPD-13	22.3	63.4	7.4		5.0 Fe		1.9	
WPD-14	55.1	30.4			5.0 Fe		9.5	
WPD-15				95 WPH-2	5.0 Cu			
WPD-16	23.0	53.0		20 CuO			4.0	

(1) SCORE Formulation

TABLE B-4

ANODE MIXES (L SERIES)

POWDER	% SALT	% K_2CrO_4	% OTHER	% OTHER	% CAB-O-SIL	NOTES
L-1	30		70 Li-Al (60 a/o Li)			
L-2	50		50 Li-Al (60 a/o Li)			
L-3	10		90 Li-Al (60 a/o Li)			
L-4	30		70 Li-Al (45 a/o Li)			
L-6	10		90 Li-Al (45 a/o Li)			
L-7	30		70 Li-Si (58 w/o Si)			
L-8	10		90 Li-Si (58 w/o Si)			
L-10	8.5		90 Li-Al (45 a/o Li)		1.5	
L-11			50 L-6	50 L-3		
L-12	10		90 Li-Al (55 a/o Li)			
L-13			80 Li-Al (45 a/o Li)	20 C		
L-14	8.1		91.9 L-13			

a/o = Atomic percent
w/o = Weight percent

TABLE B-5

NEW DEPOLARIZER MIXES (WPN SERIES)
FOR TWO LAYER SYSTEMS

POWDER	% SALT	% K_2CrO_4	% OTHER	% OTHER	% OTHER	% CAB-O-SIL	NOTES
WPN-1	25		73 $ZnCrO_4$			2	
WPN-2	23		75 $ZnCrO_4$			2	
WPN-3	23		70 NiO			7	
WPN-4	23		70 CuO			7	
WPN-5	30		63 NiO(black)			7	
WPN-6	30		63 CuO			7	
WPN-7	30		59.85 NiO	3.15 C		7	
WPN-8	30		59.85 CuO	3.15 C		7	
WPN-9	44		54 WO_3			2	
WPN-10	35		63 WO_3			2	
WPN-11	35		63 U_2O_5			2	
WPN-12	25		75 FeS_2				
WPN-13			26 $NaAlCl_4$	16 C	58 $MoCl_5$		
WPN-14			26 $NaAlCl_4$	16 C	58 $CuCl_2$		
WPN-15			26 $NaAlCl_4$	16 C	58 $FeCl_3$		
WPN-16	25		75 Fe_2O_3				
WPN-17	15		85 FeS_2				
WPN-18	40		60 FeS_2				
WPN-19	23.4		58 $CuCl_2$	16 C		2.6	
WPN-20	23.4		58 $FeCl_3$	16 C		2.6	
WPN-21	60		40 Fe_2O_3				
WPN-22	40		56 NiO			4	
WPN-23	40		56 CuO			4	
WPN-24	50		48 WO_3			2	
WPN-26	45		55 Fe_2O_3				
WPN-27	40		60 Cu_2S				
WPN-28	34		66 Cu_2S				

TABLE B-5

NEW DEPOLARIZER MIXES (WPN SERIES)
FOR TWO LAYER SYSTEMS

POWDER	% SALT	% K_2CrO_4	% OTHER	% OTHER	% OTHER	% CAB-O-SIL	NOTES
WPN-30	40		60 MnO_3				
WPN-31	16		64 FeS_2		20 WPE-16		
WPN-33			66 FeS_2		34 WPE-12		
WPN-34	34		66 FeS_2				
WPN-35	55		45 FeS_2				
WPN-36	26		60 FeS_2		14 $LiCl$		
WPN-37	26		60 FeS_2		14 KCl		
WPN-38			60 FeS_2		40 WPE-13		
WPN-39	34.4		60 FeS_2		5.6 $LiCl$		
WPN-40	19.3		60 FeS_2		20.7 $LiCl$		
WPN-41	34		59.4 FeS_2	6.6 C			
WPN-42	34		59.4 FeS_2		6.6 Cu_2S		
WPN-43	34		59.4 FeS_2		6.6 CoS_2		
WPN-44			43.6 $CuCl_2$	18.2 C	38.2 $NaAlCl_4$		
WPN-45	33.3		64.7 FeS_2	2 S			
WPN-46	39.2		58.8 FeS_2	2 S			
WPN-47	32.3		62.7 FeS_2	5 S			
WPN-48	38		57 FeS_2	5 S			
WPN-49			2 $LiAl$ (60 a/o Li)				
WPN-50			60 FeS_2		40 WPE-9		
WPN-52	39.2		58.8 FeS_2	2 Fe			
WPN-53	39.8		59.7 FeS_2		0.5 $LiAl$ (60 a/o Li)		
WPN-54	40		60 FeS_2^*				
WPN-55	40		30 FeS_2		30 FeS_2^*		
WPN-56	40	5	55 FeS_2				
WPN-57	40	2	58 FeS_2				

*New source of FeS_2

TABLE B-5

NEW DEPOLARIZER MIXES (WPN SERIES)
FOR TWO LAYER SYSTEMS

POWDER	% SALT	% K ₂ CrO ₄	% OTHER	% OTHER	% OTHER	% CAB-O-SIL	NOTES
WPN-60	40		54 FeS ₂		6 CuCl ₂		
WPN-61	40		54 FeS ₂		6 FeCl ₂		
WPN-62	40		6 Fe ₂ O ₃		54 FeS ₂		
WPN-63	40		6 MnO ₂		54 FeS ₂		
WPN-64	40		30 Fe ₂ O ₃		30 FeS ₂		
WPN-65	40		60 FeS				
WPN-66	40		30 FeS ₂		30 FeS		
WPN-67	39.6	1	59.4 FeS ₂				
WPN-68	38		57 FeS ₂		5 Fe		
WPN-69	39.8	0.5	59.7 FeS ₂				
WPN-70	40		45 FeS ₂	6.3 CoS	8.7 CoS ₂		
WPN-71	50		50 FeS				
WPN-72	30		70 FeS				

APPENDIX C

PHYSICOCHEMICAL STUDIES

Physicochemical studies included physical, chemical, and thermal analysis of individual powders and mixtures. These studies were made in order to standardize materials and establish quality control.

Physical analysis of incoming raw materials was used to determine the particle size of these materials. It was especially important to monitor and subsequently control the particle size of CaCrO_4 before and after mixing. It was found, for example, that after mixing, the particle size of CaCrO_4 in the mix was not randomly distributed.

Chemical analysis monitored the purity of incoming raw materials. Electrolyte materials were reagent grade but were chemically analyzed. LiCl-KCl was analyzed after each compound was dried to remove water, mixed in the desired weight ratio, fused, and ground to the proper size.

Calcium, magnesium, and lithium anode materials were obtained in sheet form, 10 mil, 17 mil, and 10 mil, respectively. They were used as received after they were cleaned of the oil in which they were stored for shipment. The alloys of lithium-aluminum and lithium-silicon were received in granular form sealed under argon and were used as received.

Cathode materials were reagent grade chemicals and were also used as received. Where these materials contained water of hydration, it was adequate to remove this water by drying at a temperature in excess of 150°C .

CHEMICAL STUDIES

These studies were undertaken to reinforce the thermographic data and electrochemical studies. The components of the electrochemical cell -- calcium, eutectic KCl-LiCl , and CaCrO_4 -- were studied primarily for purity.

Calcium. Calcium metal "as received" was observed to be covered with a film ranging from light grey to dark brown in color. The edges of freshly cut calcium were silvery grey. To find the composition of the film, it was scraped off and analyzed for the calcium content. The following observations were made:

Ca % by volumetric analysis	47.17
Ca % by atomic absorption	57.60

If the film were assumed to be a mixture of CaO and Ca_3N_2 , this analysis could be readily explained. Conclusive proof for the presence of nitride has not yet been established.

Calcium Chromate. Calcium chromate, depending on the method of manufacture, contained one or more of the following impurities: CaCO_3 , Ca(OH)_2 , CrO_3 , Cr_2O_3 , and H_2O . Table C-1 shows the wide variation observed in "as received" material. Incoming CaCrO_4 was analyzed for chromium and calcium content using iodometry and atomic absorption. Furthermore, Cr_2O_3 , CrO_3 , and H_2CrO_4 were added as impurities to calcium chromate in order to study their effect on chemical analysis and thermal behavior. Table C-2 indicates the results of chemical analysis. In general, it can be concluded that the addition of Cr_2O_3 resulted in the lowering of the calcium chromate purity and increased the concentration of the product of reaction in cells. The addition of CrO_3 , however, resulted in increased purity since it increased the Cr(VI) without drastically affecting the thermal behavior observed by means of differential scanning calorimetry.

Eutectic Mixture of KCl-LiCl . The eutectic salt mixture contains 44.5 weight-percent KCl and 55.5 weight-percent LiCl . The mixture was analyzed for chlorine content by volumetric analysis and, assuming 100% purity of LiCl-KCl , the composition was determined by atomic absorption. The composition of the salt mixture was thus controlled.

THERMAL STUDIES

Thermal studies were conducted using a differential scanning calorimeter (Perkin-Elmer DSC-2) to record the enthalpy change involved in heating and cooling a substance between 40°C and 720°C . These studies were made to determine the effects of heating different components and mixtures and to observe phase changes or reactions involved at elevated temperatures.

Calcium. Various samples of available calcium were scanned for their thermal behavior and the following conclusions were drawn:

An endotherm was observed on the heating curve of a freshly cut calcium sample at temperatures ranging between 320° and 340°C . This endotherm was attributed to an allotropic phase change and its temperature depended upon the purity of the sample. This agreed with observations stated in the literature.

TABLE C-1
VARIATIONS IN AS-RECEIVED CALCIUM CHROMATE

LOT NO.	PERCENTAGE CALCIUM CHROMATE			DSC FIG. NO.
	IODOMETRY	ATOMIC ABSORPTION		
	Cr (VI)	Ca	Cr	
8202-2	95.1	94.6	92.6	C 1
8202-11	98.9	93.0	97.6	C 2
8058	96.0	97.5	93.2	C 3
7619	87.0	109.1	83.5	C 4
G-219	98.3	-		C 5
G-301	99.1	-	99.2	C 6
MP	84.6	102.0	86.4	C 7

TABLE C-2

EFFECT OF IMPURITIES ON CALCIUM CHROMATE
(LOT 8202-2)

	PERCENTAGE CALCIUM CHROMATE			DSC FIG. NO.
	IODOMETRY	ATOMIC ABSORPTION		
	Cr (VI)	Ca	Cr	
1. As Received	95.1	94.6	92.6	C 1
2. Add 2 Wt% CrO ₃	99.7	89.8	96.7	C 8
3. Add 2 Wt% Cr ₂ O ₃	92.7	91.0	93.3	C 9
4. Add H ₂ CrO ₄	95.7	93.8	93.7	C 10

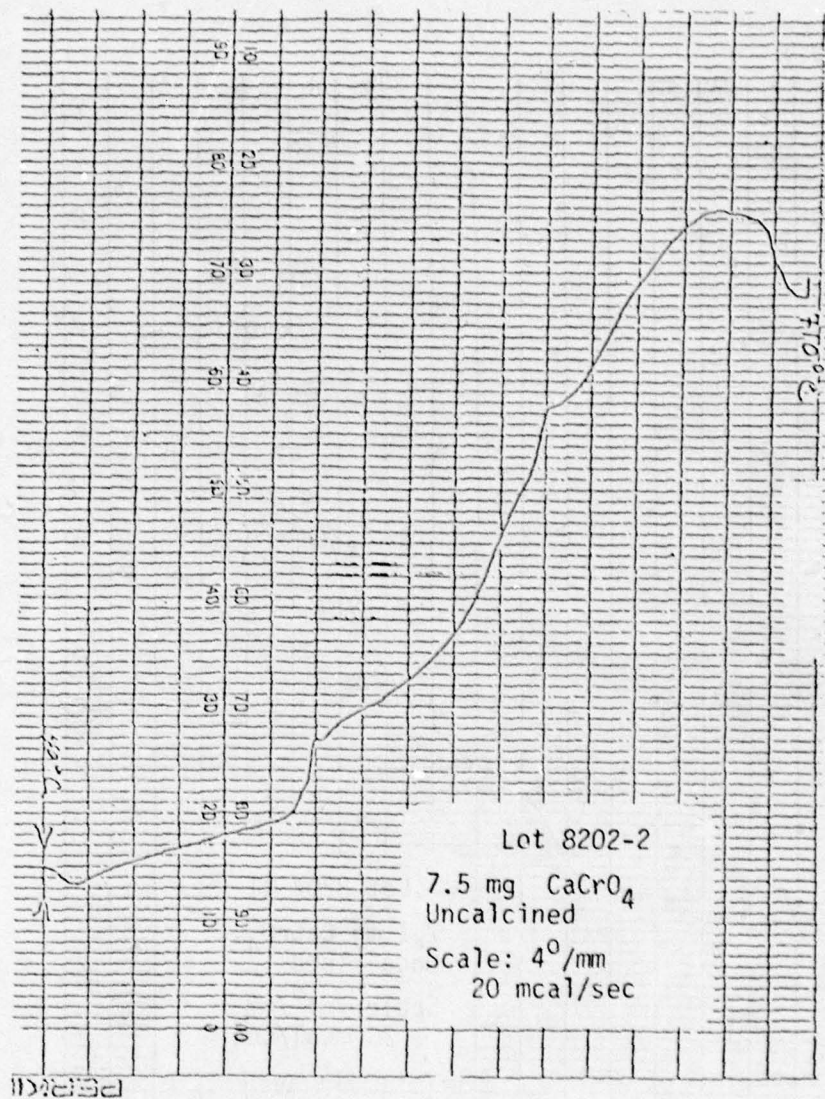


Figure C-1. Heating Curve for CaCrO₄ - Lot 8202-2

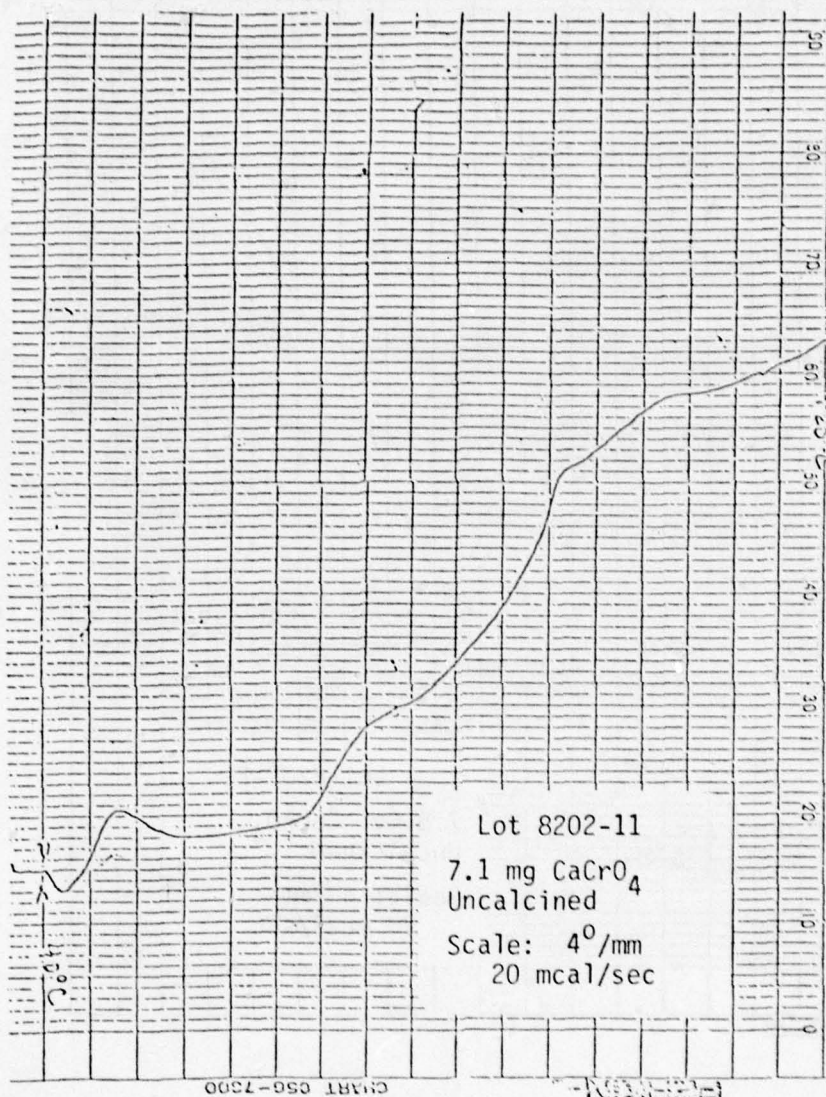


Figure C-2. Heating Curve for CaCrO_4 - Lot 8202-11

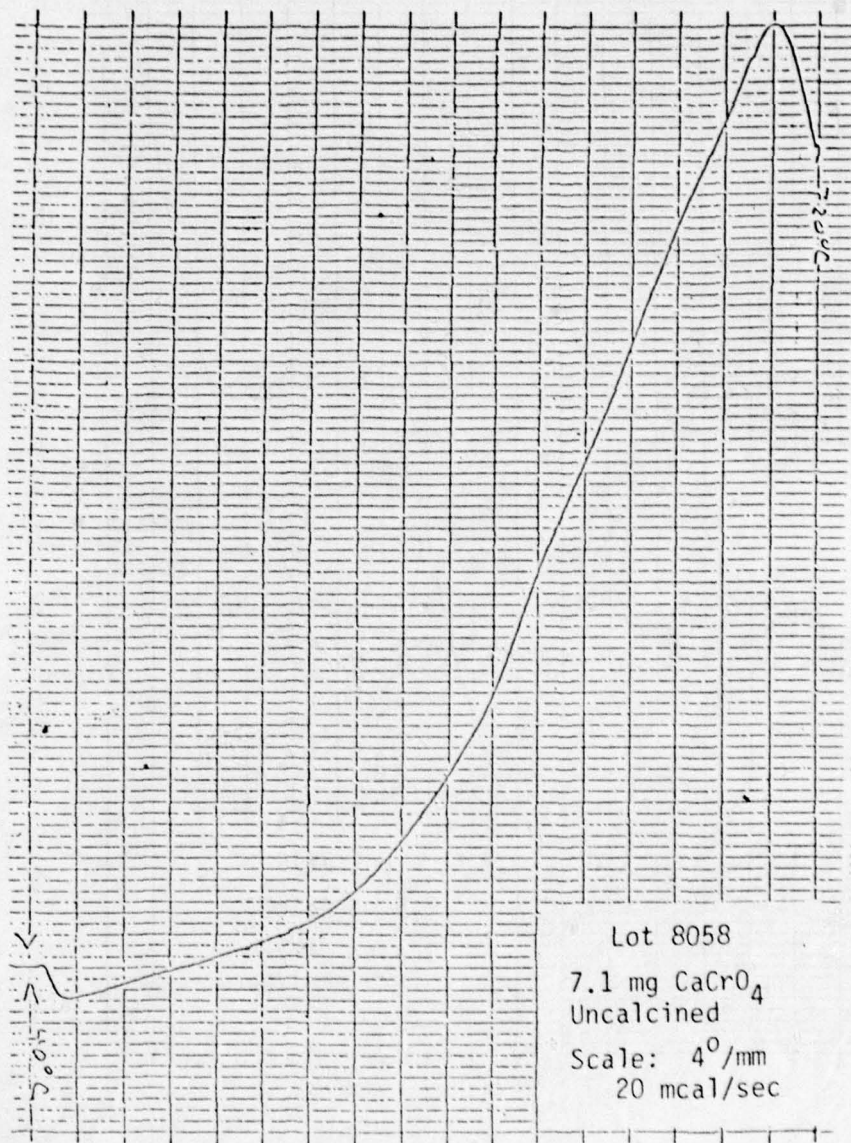


Figure C-3. Heating Curve for CaCrO_4 - Lot 8058

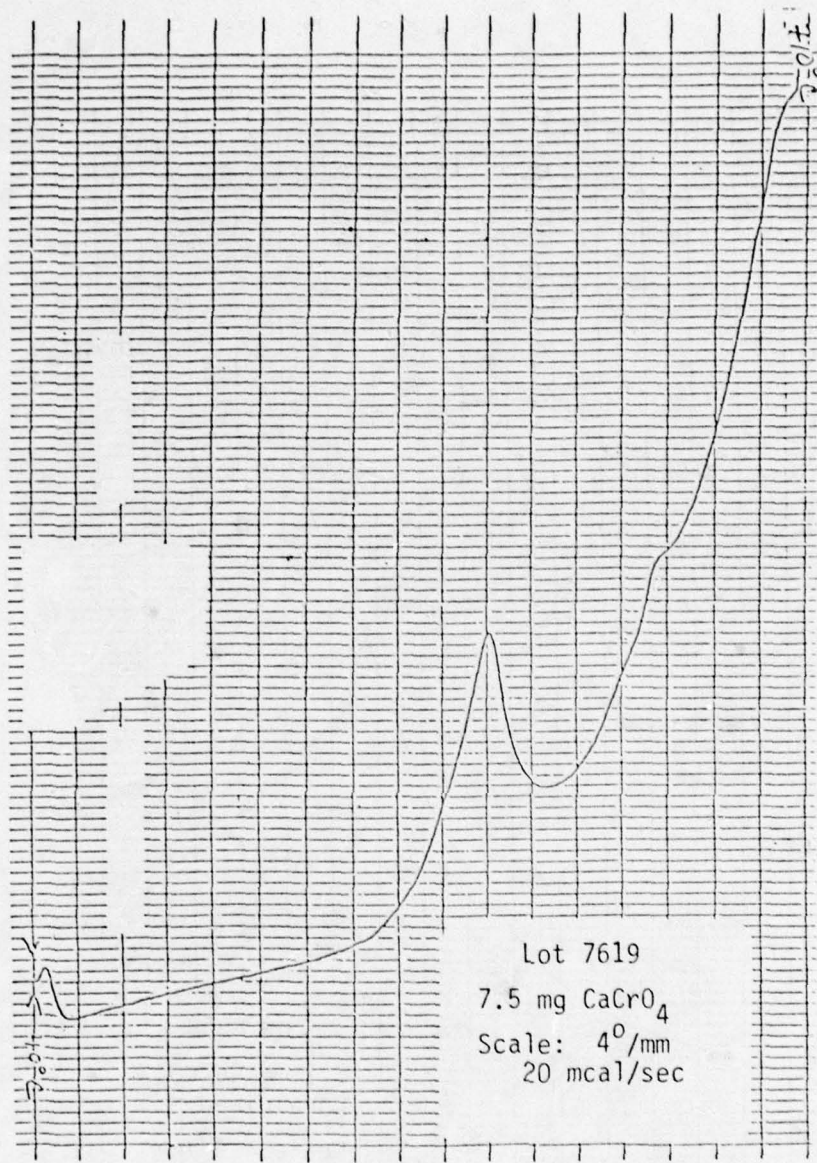


FIGURE C-4

Figure C-4. Heating Curve for CaCrO_4 - Lot 7619

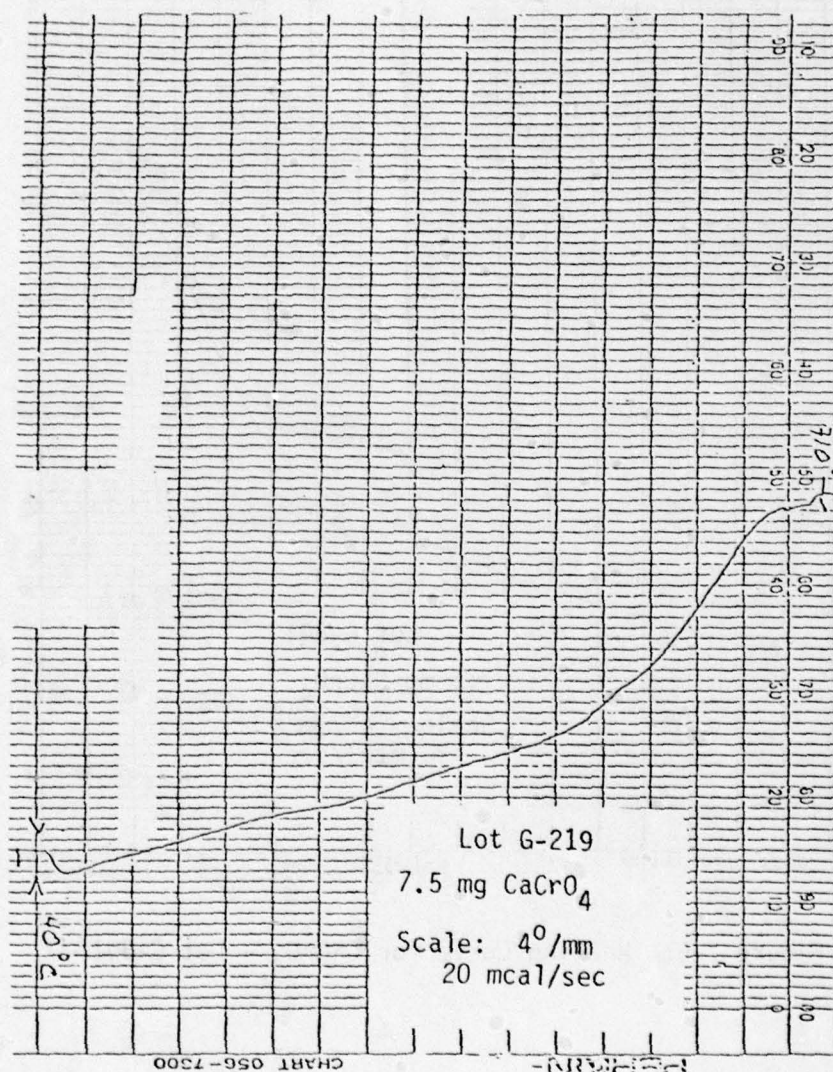


Figure C-5. Heating Curve for CaCrO_4 - Lot G-219

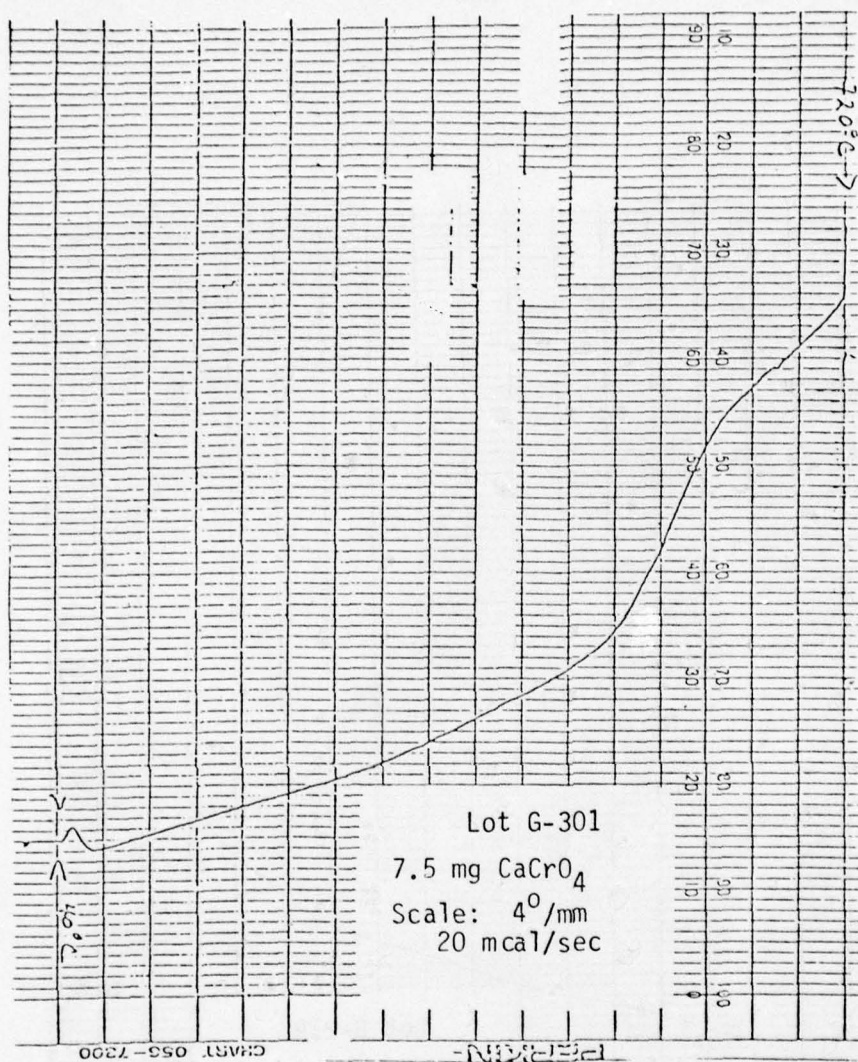


Figure C-6. Heating Curve for CaCrO_4 - Lot G-301

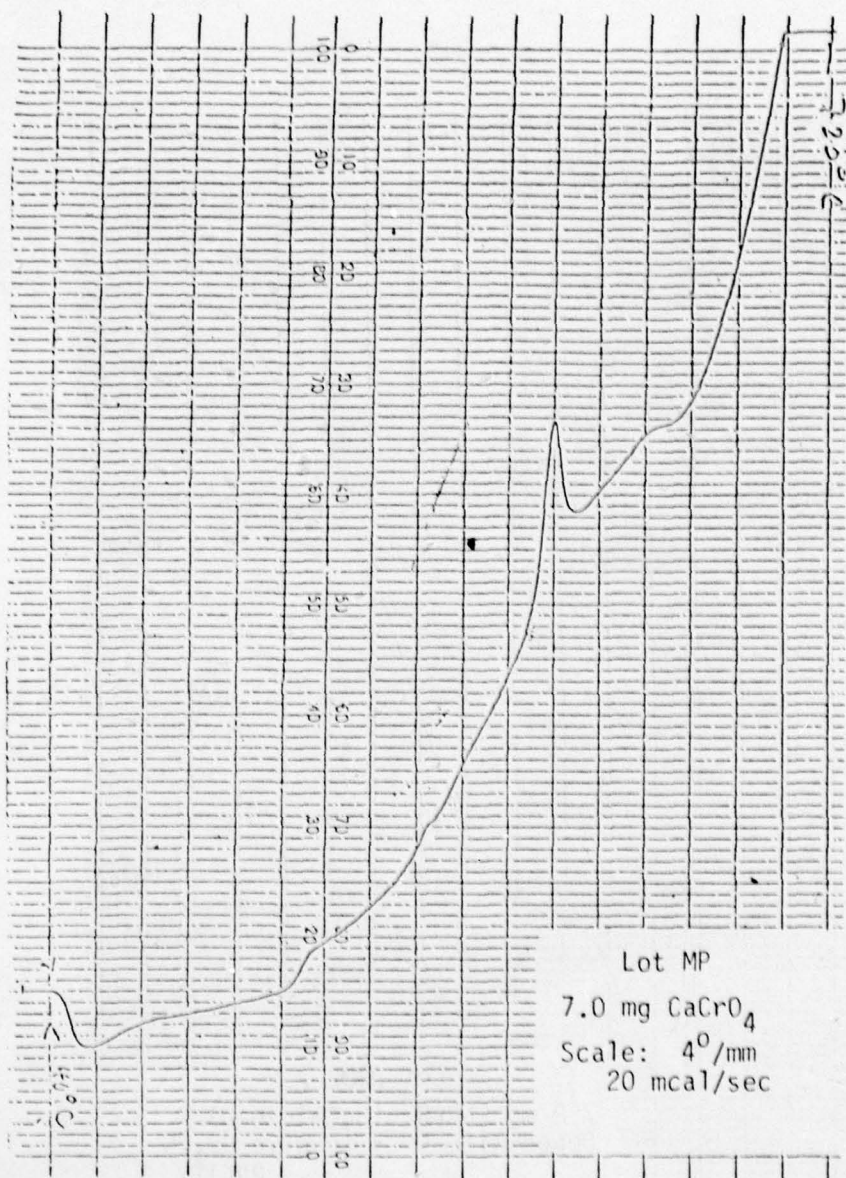


Figure C-7. Heating Curve for CaCrO_4 - Lot MP

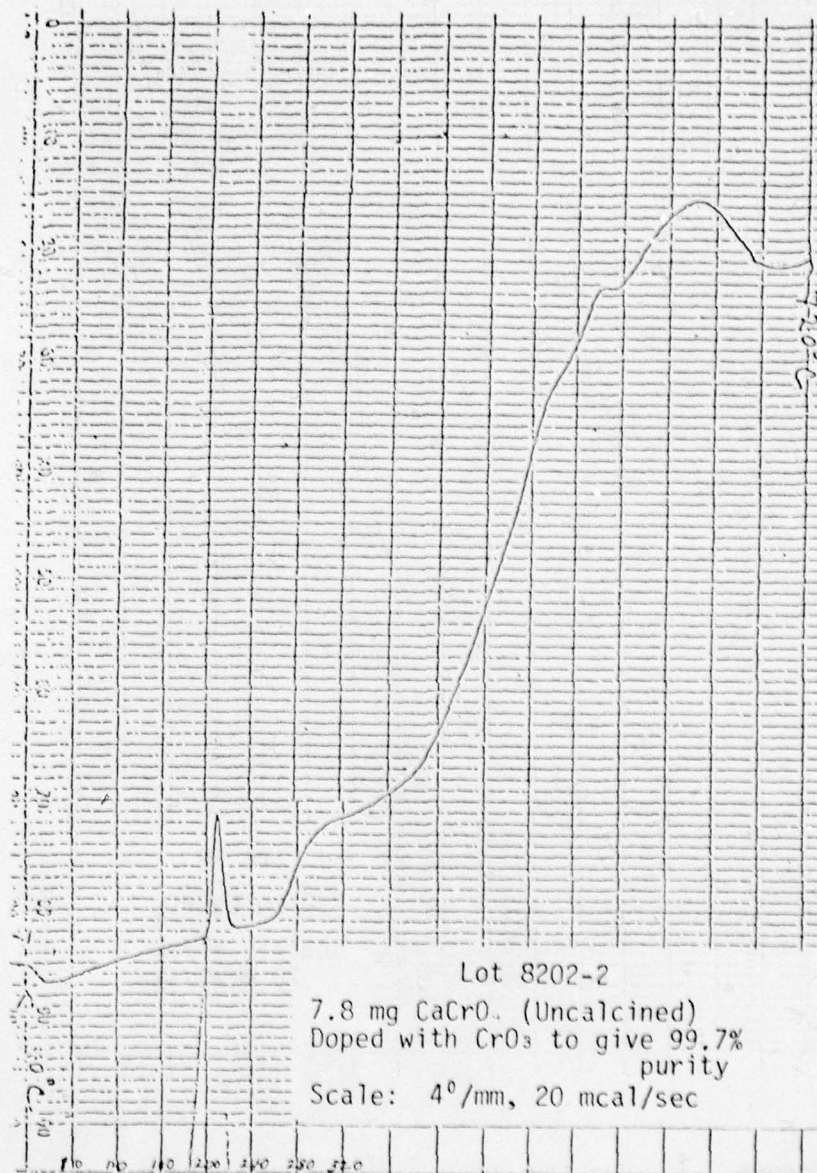


Figure C-8. Heating Curve for CaCrO_4 - Lot 8202-2

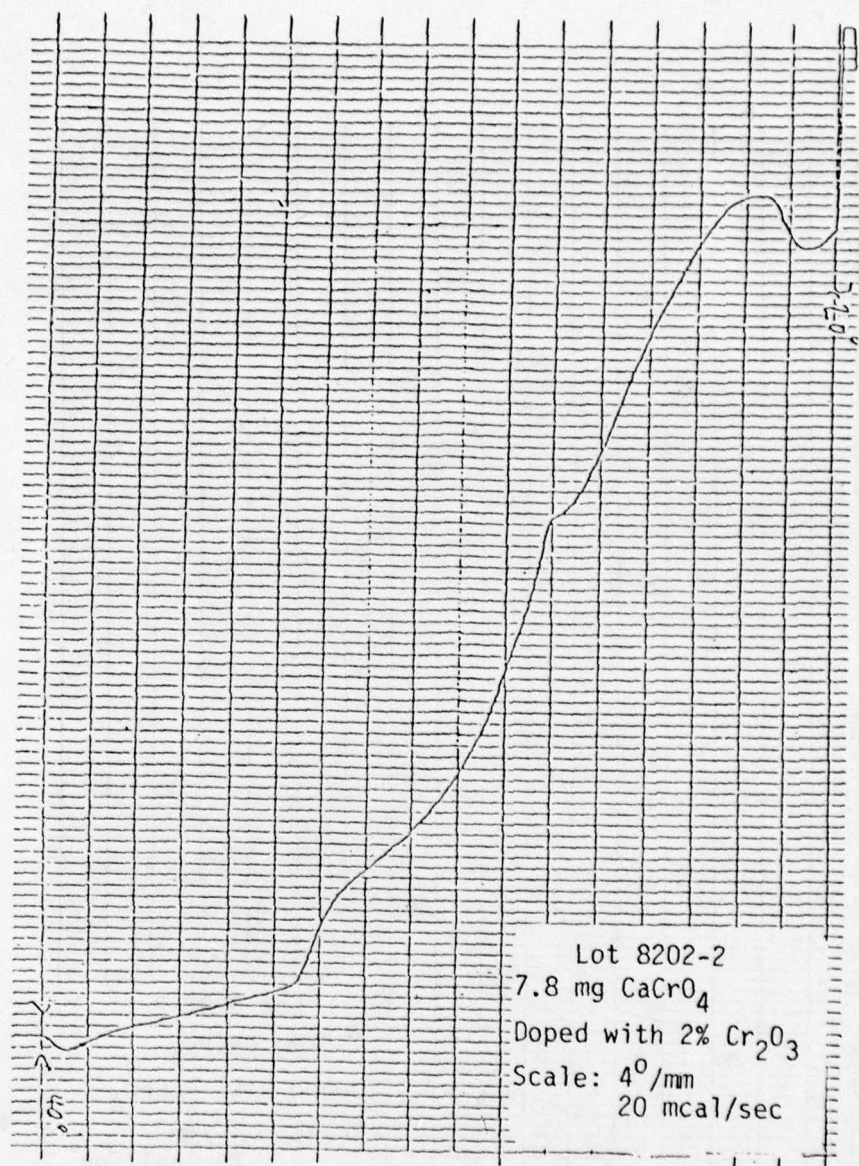


Figure C-9. Heating Curve for CaCrO_4 - Lot 8202-2

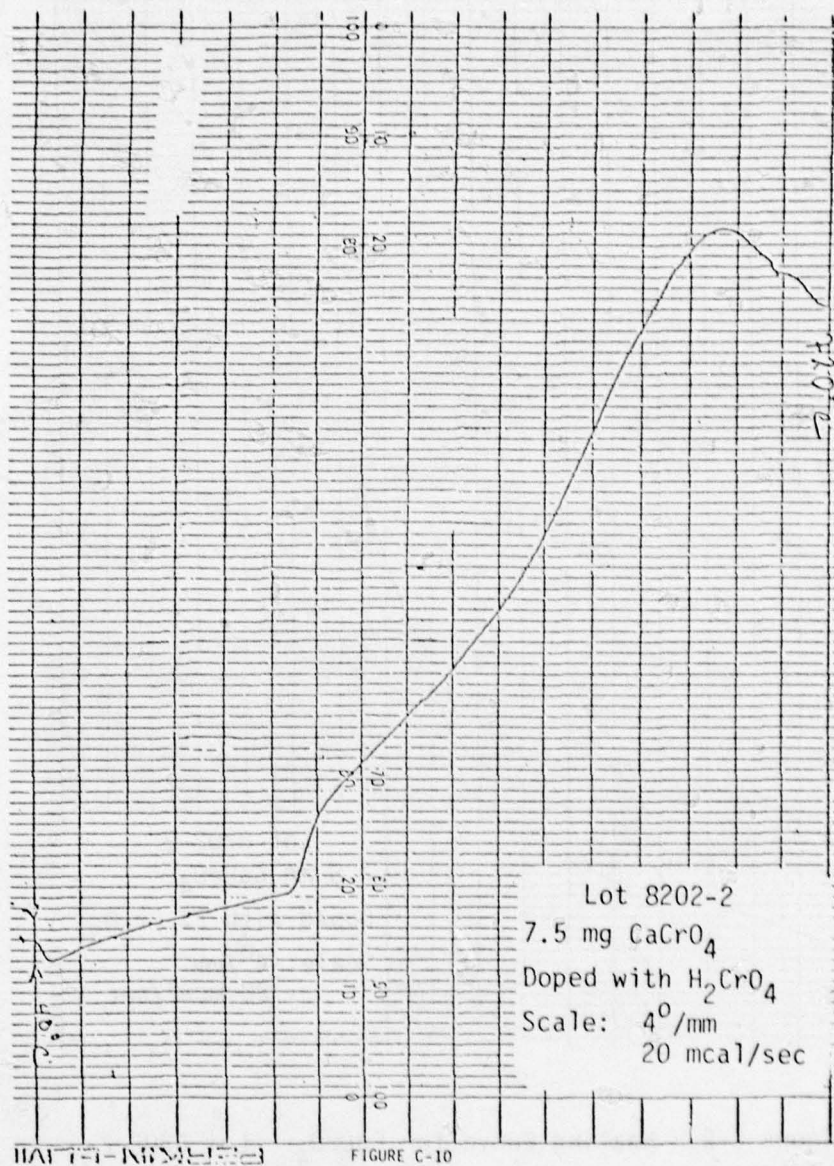


Figure C-10. Heating Curve for CaCrO_4 - Lot 8202-2

Depending on storage conditions and duration, the calcium had a coating which was metallic grey to dark brown. These samples exhibited an exothermic change at about 300°C . This indicated the presence of $\text{Ca}(\text{OH})_2$. In order to study the nature of this film it was scraped off the calcium surface. Thermal analysis of the particles revealed a highly exothermic phenomena at about 200°C indicating formation of $\text{Ca}(\text{OH})_2$ from CaO . The endotherm at 340°C was due to both allotropic phase change of calcium and dissociation of $\text{Ca}(\text{OH})_2$. Upon reheating this sample, no further changes were observed.

When a sample of calcium was placed in a humid atmosphere, a light grey film formed on its surface. This was assumed to be $\text{Ca}(\text{OH})_2$. Heating a sample of this material showed the absence of both the exothermic peak and the endotherm at 340°C .

By the methods described, it is possible to identify certain types of contamination on calcium. It has been confirmed at KDI SCORE that battery noise (due to CaLi_2 bridging) may be prevented by exposing the calcium edges to moisture. This study helped to interpret and standardize the process.

Calcium Chromate. Thermal studies of CaCrO_4 revealed some startling results. As indicated in Table C-3, heating CaCrO_4 increased its hexavalent chromium content by approximately 2%. Initially, this is due to loss of moisture and later to dissociation of CaCO_3 and $\text{Ca}(\text{OH})_2$. However, at higher temperatures, the CaCrO_3 itself partially decomposed. The thermogram indicates that the heat requirement for this sample is reduced by almost 50% compared with that for untreated CaCrO_4 . This would have considerable effect on the thermal requirement for batteries where the aim is to minimize caloric input.

Heat Paper. Heat paper is composed of a mixture of Zr (20-30%) and BaCrO_4 blended with fibers to control the calorific value and ignition sensitivity. The thermal study of the individual components led to the following observations:

- 1) The glass fibers required a preheat treatment to about 400°C to remove volatile impurities.
- 2) The Zr-BaCrO_4 mixture became inactive if heated to 340°C where Zr was converted to ZrO_2 . This was indicated by an exotherm on the thermogram.
- 3) Slurry samples from various batches exhibited differences on thermograms indicating composition variations among batches.

TABLE C-3

EFFECT OF HEAT ON CaCrO_4 FROM LOT NO. 8202-2

	TEMP. °F	TIME (HRS.)	IODOMETRY %	ATOMIC ABSORPTION		DSC FIG.NO.
				Ca%	Cr%	
1) Uncalcined	-	-	94.96	94.6	92.6	
2) Calcined	450	3	95.4	95.2	93.6	C-11
3) Calcined	450	16	96.73	94.88	93.55	
4) Calcined	753	4	97.98	96.66	94.7	C-12
5) Calcined	753	6	97.90	96.0	94.3	
6) Calcined	753	16	97.97	94.88	93.55	
7) Calcined	1000	0.5	97.43	97.13	94.36	
8) Calcined	1400	0.5	97.26	98.48	94.04	C-13
9) Calcined	1800	0.5	91.22	97.04	92.78	

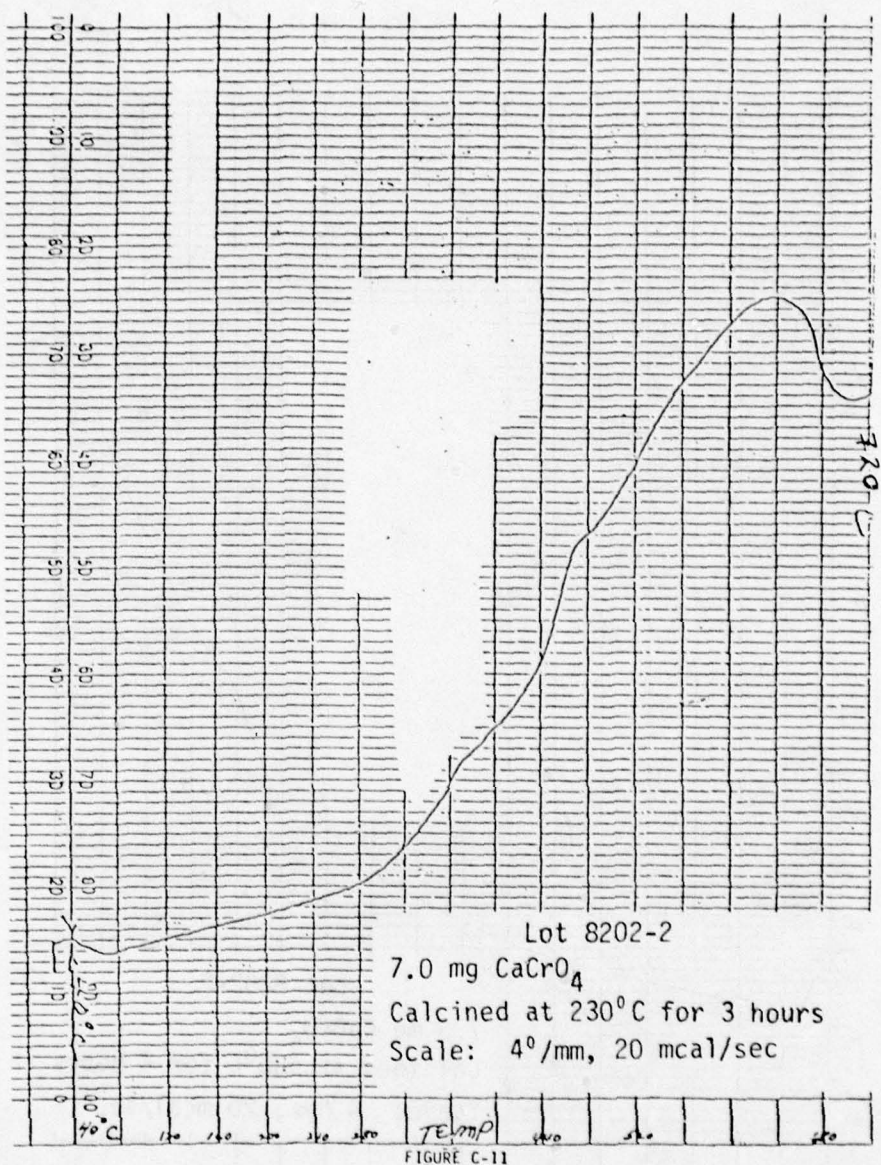


Figure C-11. Heating Curve for CaCrO_4 - Lot 8202-2

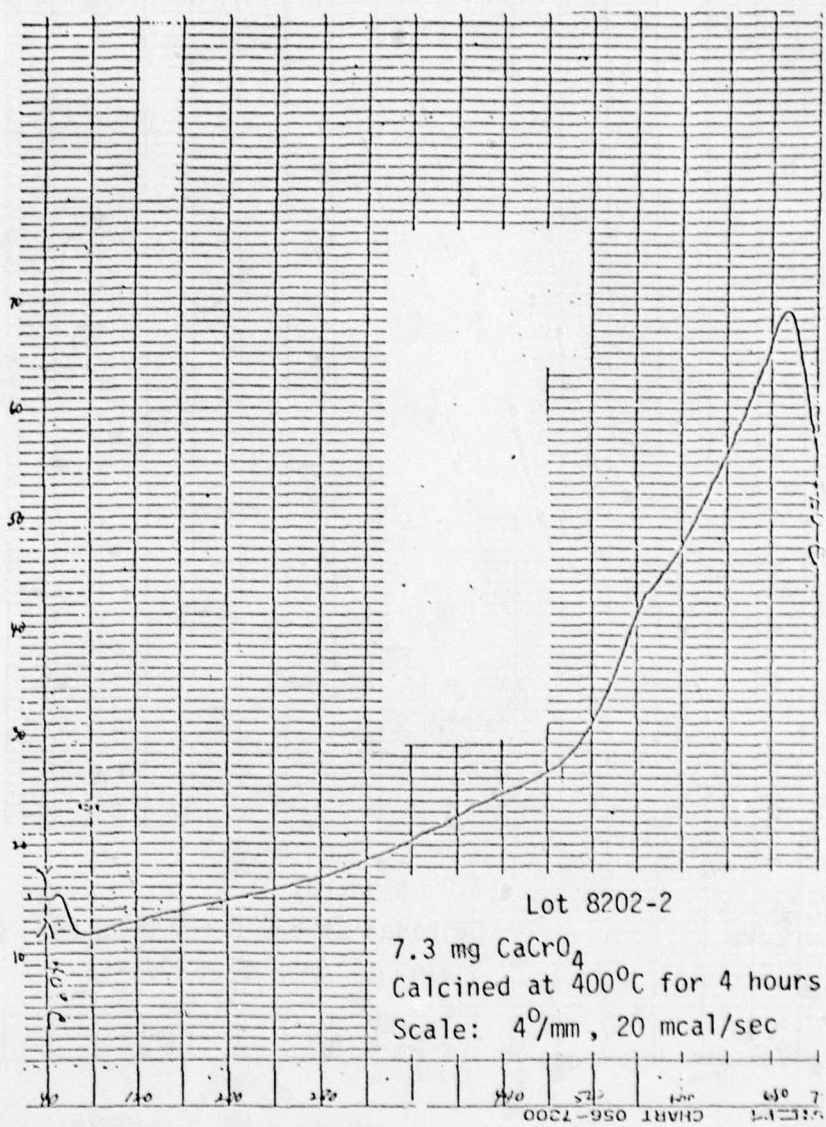


Figure C-12. Heating Curve for CaCrO_4 - Lot 8202-2

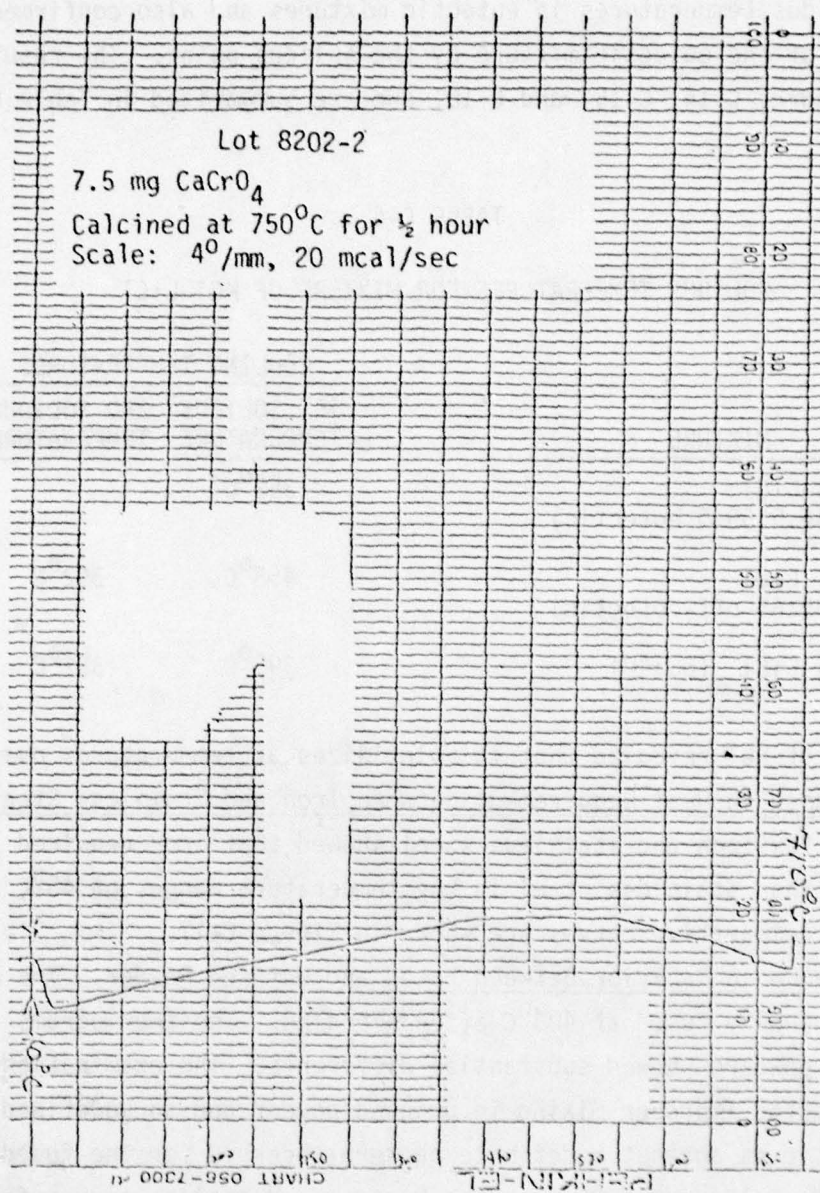


Figure C-13. Heating Curve for CaCrO_4 - Lot 8202-2

Eutectic Mixture of KCl-LiCl (44.5:55.5). Thermal studies of eutectic and non-eutectic salt mixtures clearly indicated a means of controlling their compositions. Cooling curves of the salt mixtures clearly indicated the two solidus temperatures in eutectic mixtures and also confirmed the composition of the eutectic mixture by the solidus point. The results are shown in Figures C-14, C-15, and C-16, and are summarized in Table C-4 below.

TABLE C-4

SOLIDUS TEMPERATURES FOR MIXTURE OF KCl-LiCl

MIXTURE	COOLING TEMPERATURES	
	1ST SOLIDUS TEMPERATURE	2ND SOLIDUS TEMPERATURE
KCl-LiCl (44.5:55.5 eutectic)	352°C	
KCl-LiCl (35:65 off-eutectic)	455°C	352°C
KCl-LiCl (60:40)	395°C	352°C

Thermograms of KCl revealed that it volatilizes at temperatures over 450°C.

Difference in Heat Requirement Between Iron and Stainless Steel. The thermograms for iron and stainless steel showed that iron required 11.6 cal/gm more than stainless steel in the temperature ranges of 40°C to 600°C. The comparative curves are shown in Figure C-17.

Difference in Behavior Between Fused and Unfused Powder. The mixed powder was usually fused at 400°C after blending. The thermograms for fused and unfused powders showed substantial difference. The examination of the curves indicated improper mixing in unfused powder and an undefined cooling characteristic as against a definite pattern observed for the fused powder. Figures C-18, C-19, and C-20 show the heating and cooling curves for one typical powder mix.

Difference in Behavior Between Pellet and Powder. No significant difference in thermal characteristics was observed between fused powder and pellets made from it.

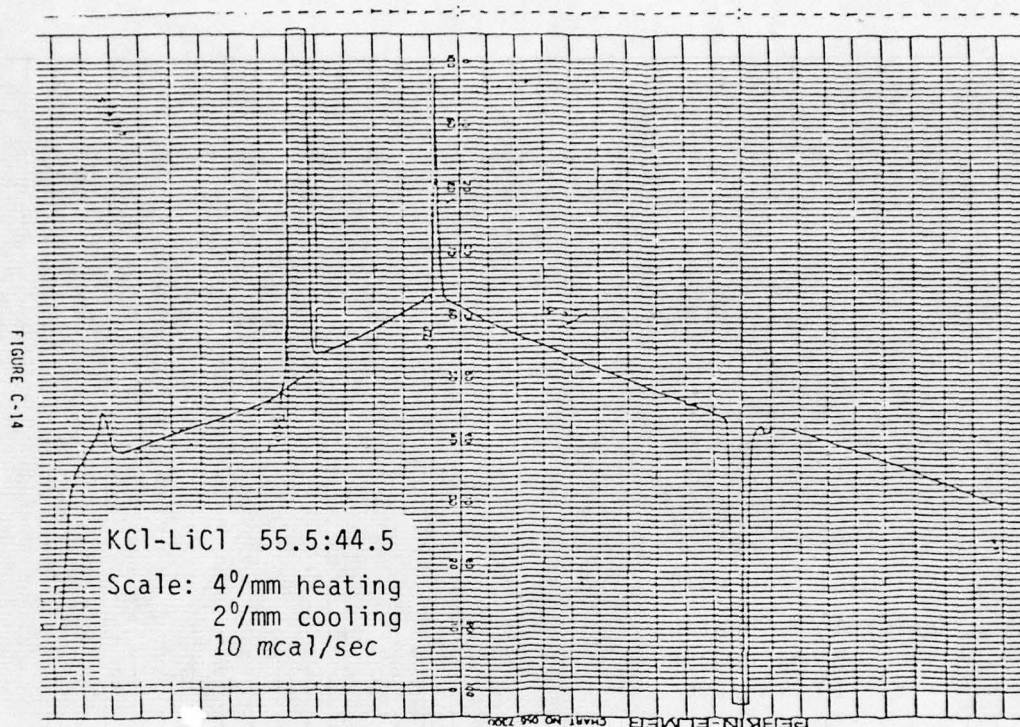


Figure C-14. DSC Thermogram for KCl-LiCl

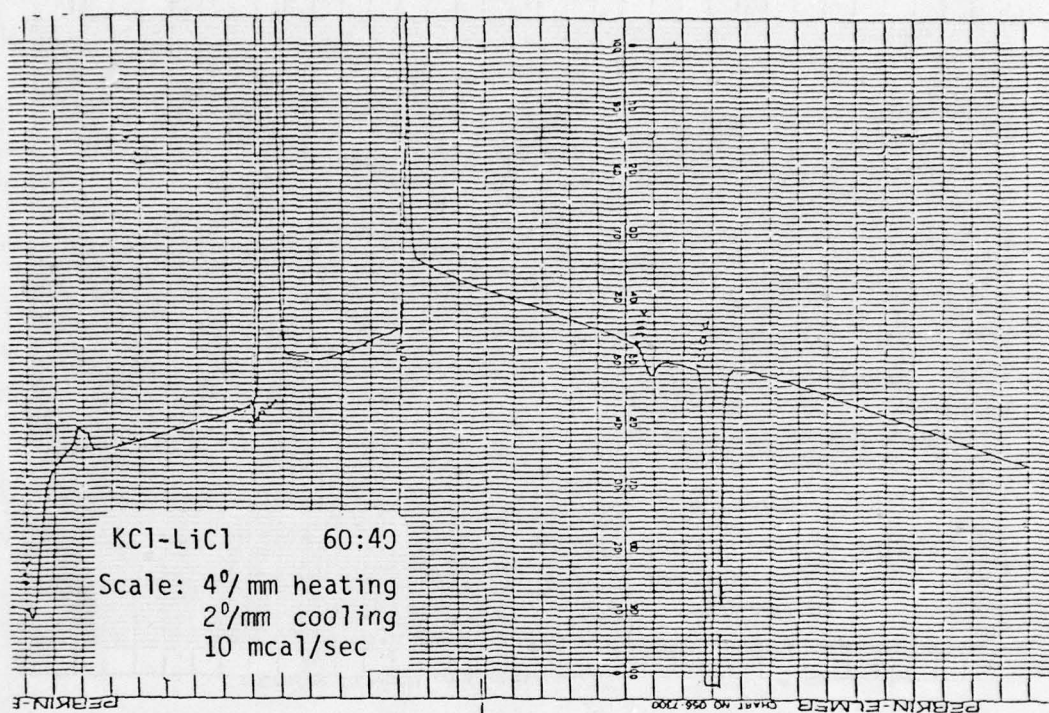


Figure C-15. DSC Thermogram for KCl-LiCl

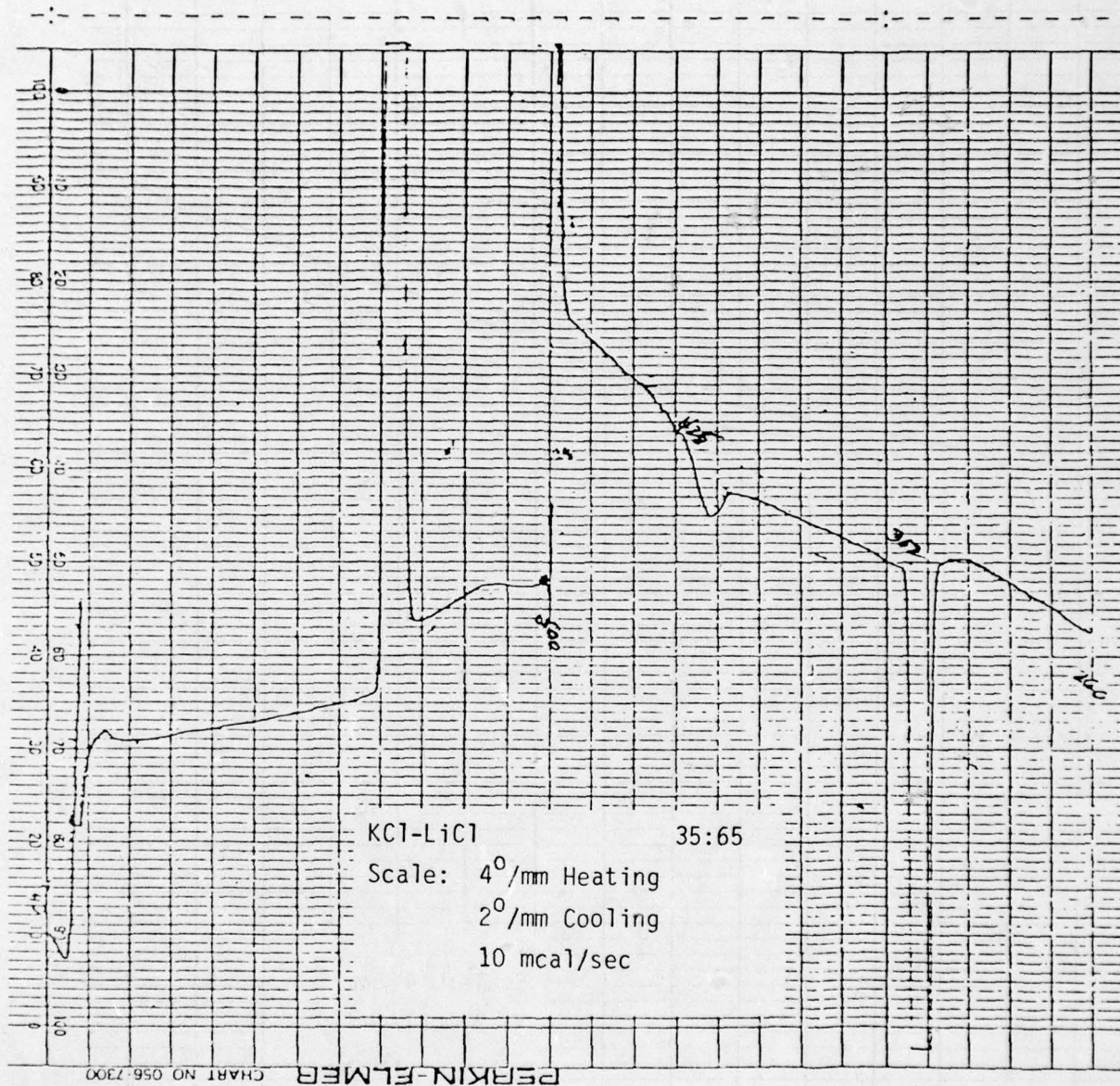


Figure C-16. DSC Thermogram for KCl-LiCl

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IMPROVED THERMAL BATTERY.(U)
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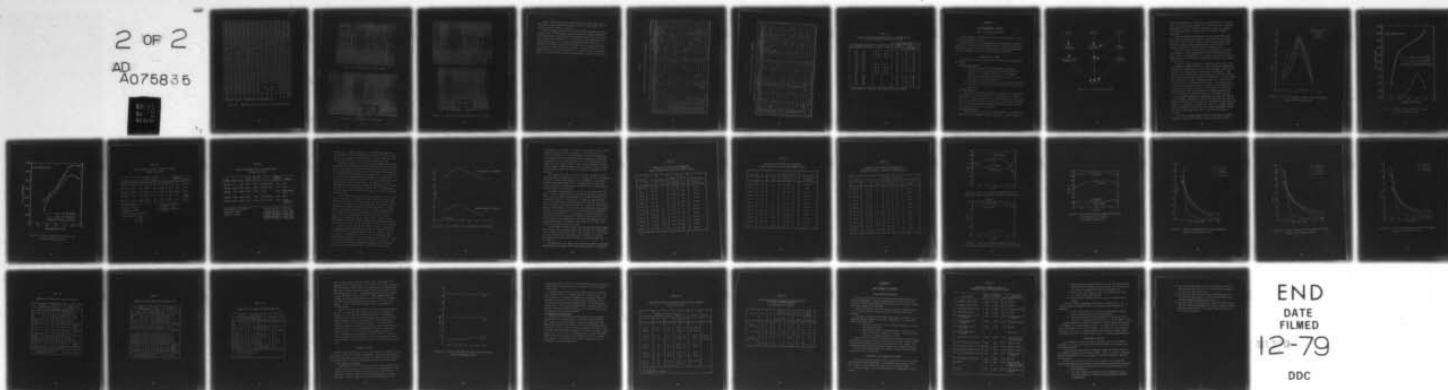
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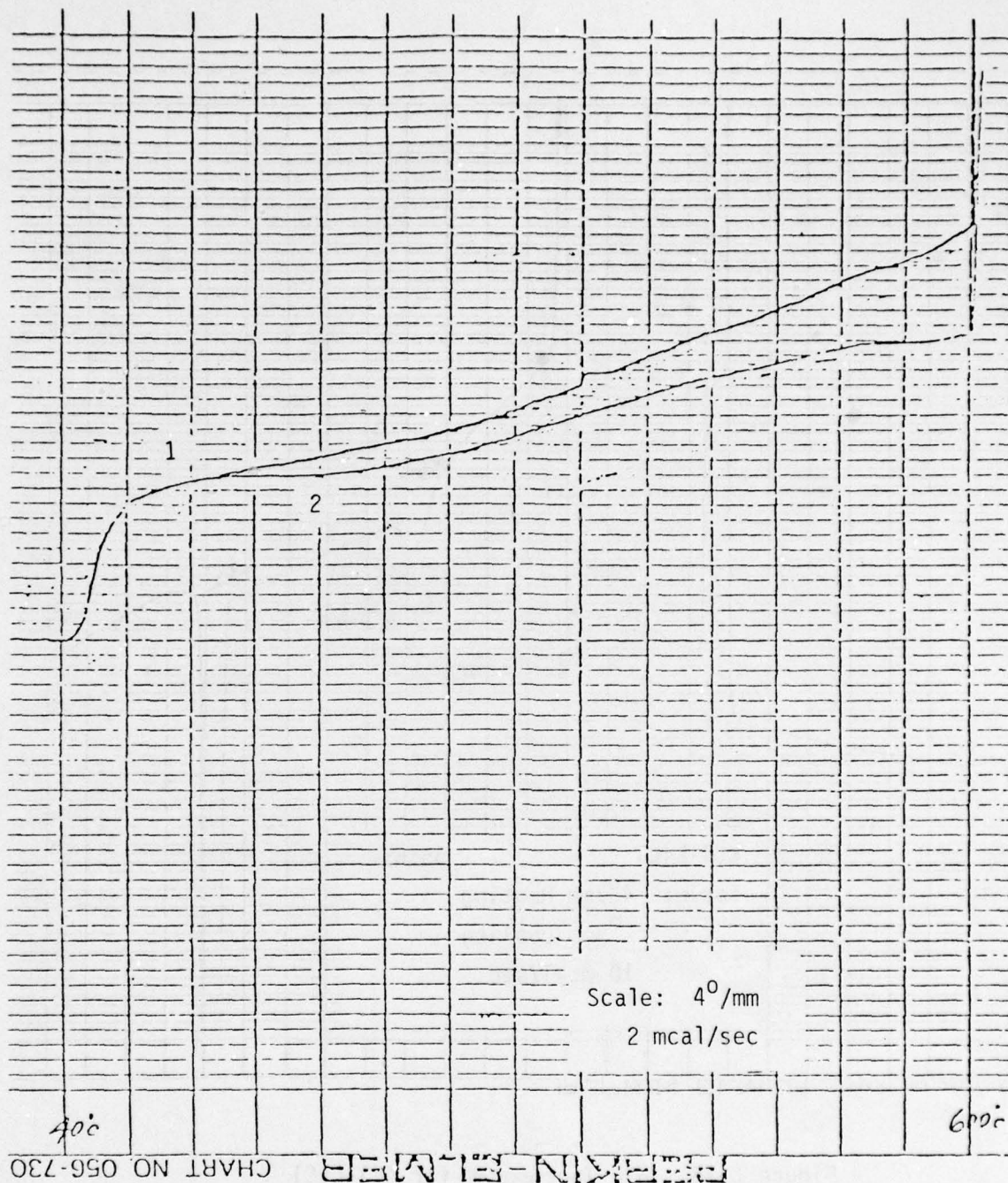


Figure C-17. Comparison Curves for Iron (1) and Stainless Steel (2)

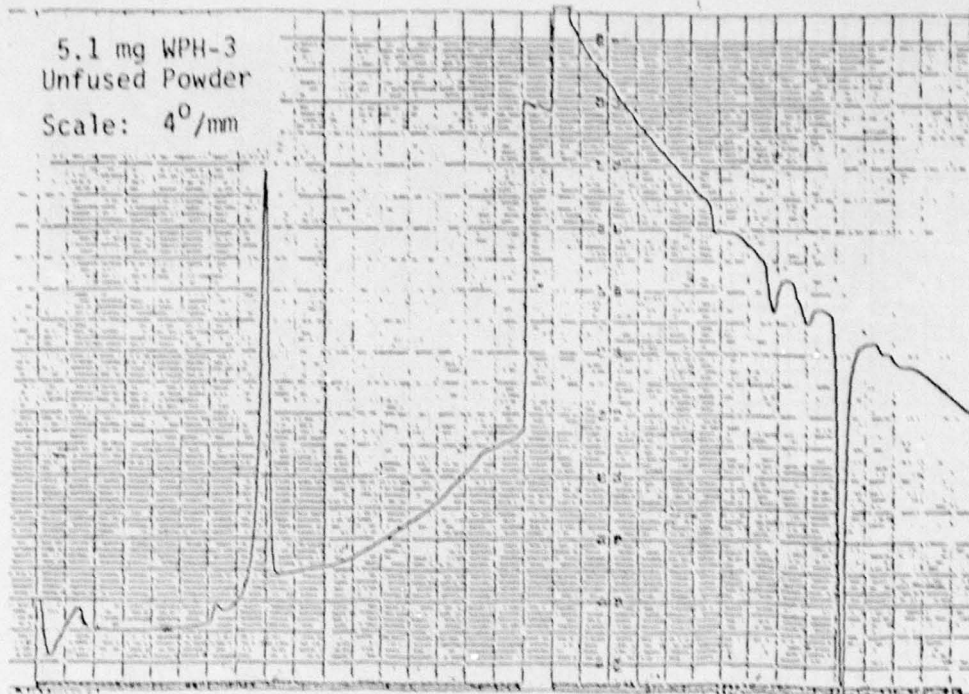


Figure C-18. DSC Thermogram for Unfused Powder

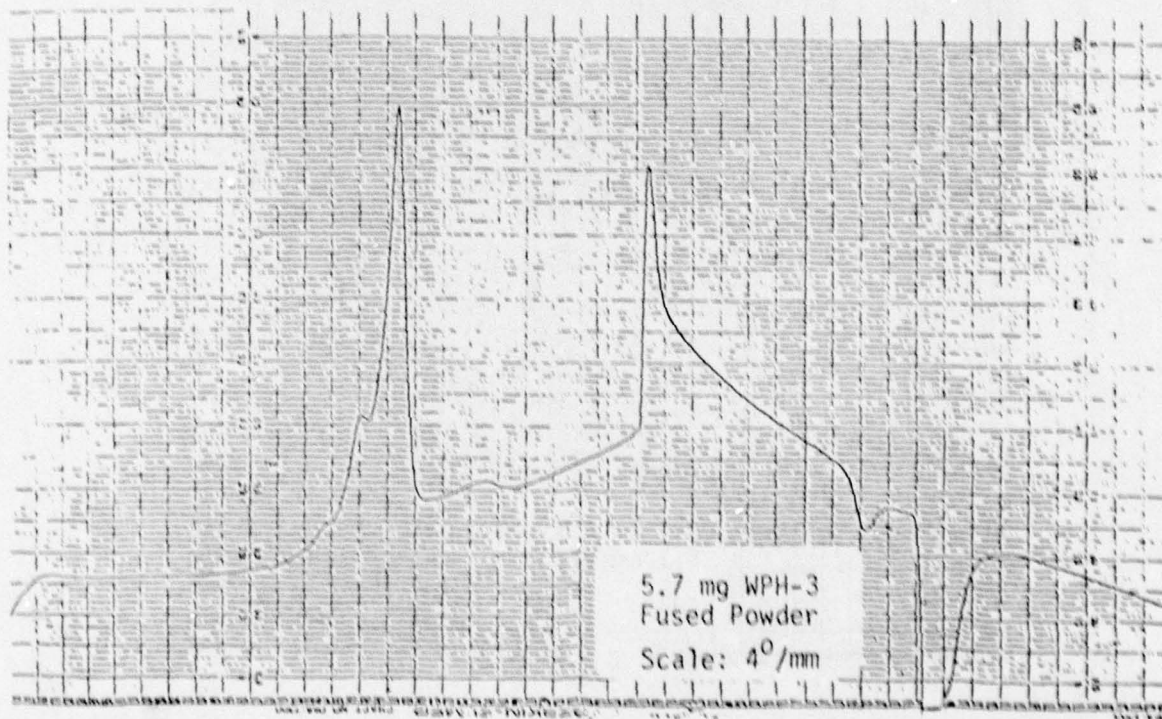


FIGURE C-19

Figure C-19. DSC Thermogram for Fused Powder

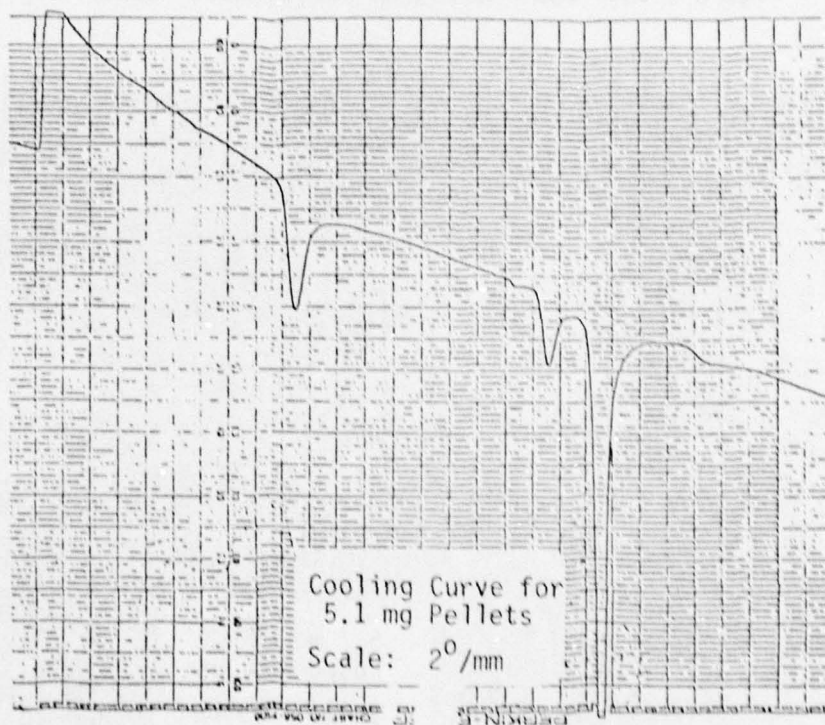
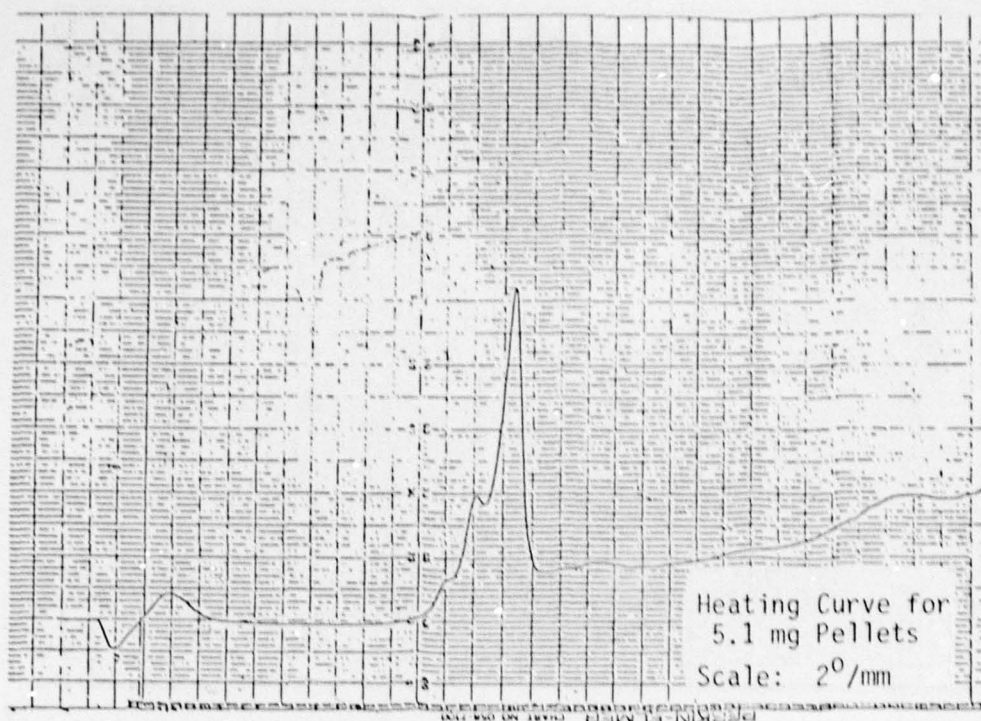


Figure C-20. Heating Curve and Cooling Curve for 5.1 mg Pellets

Thermal studies have also been conducted on KCl , LiCl , CaCrO_4 , K_2CrO_4 , PbCrO_4 , their binary and ternary mixtures, and their powder mixes. The results are given in Tables C-5 and C-6.

Table C-7 contains the results of thermal studies on WPH-2 with various particle sizes. The thermograms showed an increase of solidus temperature (on cooling) when the particle size was changed from 230 mesh U.S. Standard size to 60 mesh U.S. Standard size. A similar shift was observed when the time period of fusion was increased and also when the particle size distribution of the WPH-2 powder mix was changed; that is, when the spread of the largest to smallest particle was changed. In all of these cases, the thermal balance of the battery was affected. Modifications in the thermal analyses to include thermal conductivity measurements have been implemented.

THERMAL STUDY OF Ca/CaCrO_4 SYSTEM COMPONENT THERMOGRAMS90

TABLE C-6

THERMAL STUDY OF Ca/CaCrO_4 SYSTEM COMPONENT THERMOGRAMS

COMPONENT SYSTEMS	HEATING														COOLING																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	
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	80	120	160	200	240	280	320	360	400	440	480	520	560	600	640	680	720	720	680	640	600	560	520	480	440	400	360	320	280	240	200	160	120																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																															
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*Exotherm in heating; denotes decomposition of CrO_3

TABLE C-7

THERMAL PEAK TEMPERATURES AND RESULTS OF CHEMICAL ANALYSIS
FOR WPH-2 POWDER MIX, PARTICLE SIZE STUDY

				THERMAL PEAKS (°C)		
U.S. STANDARD SIEVE NO.		% SALT	% CaCrO_4	HEATING	COOLING	
					FIRST	SECOND
-60	+80	12.67	65.18	351	599	302
-80	+100	40.83	43.77	350	542	293
-100	+120	55.99	32.24	351	539	295
-120	+140	-	-	351	535	296
-140	+170	-	-	350	524	295
-170	+200	59.78	27.95	350	516	298
-200	+230	60.14	26.68	351	511	296
-230	+270	59.73	28.32	350	534	288
-270		57.63	31.06	-	-	-
-80	+200	-	-	358	545	296
-80	+230	-	-	357	550	300
-100	+230	-	-	357	530	296
-100	+200			357	530	297

WPH-2 Powder Mix - 58% salt, 32% CaCrO_4 , 10% SiO_2 (by weight)

APPENDIX D

ELECTROCHEMICAL STUDIES

Ca/LiCl-KCl/CaCrO₄ SYSTEM

The electrochemical studies were divided into two categories: single cell testing and battery testing.

Initial evaluations of the performance of the systems were conducted on the basis of single cell testing, and once the systems showed promising behavior with respect to life and energy density, the pellets were tested in ten cell standard batteries to obtain a direct correlation.

SINGLE CELL TESTING

Single cell testing was divided into the following areas to systemize the studies:

Chemical Formulations.

- 1) Selection, preparation, and acquisition of chemicals.
- 2) Comparison of results obtained with SANDIA and KDI SCORE DEB pellets -- homogeneous powder mixes. (The SANDIA powder mixes and pellets made from them were used as a basis for comparison with other systems).
- 3) Evaluation of simple variations of these chemical formulations.
- 4) Comparison of single layer DEB pellets with two layer (EB and DB) pellets.

Chemical Additives.

The effects of additions of potassium chromate, calcium hydroxide, lead chromate, chromium trioxide, and lithium chromate were studied. Additions of conductive powders like C (graphite), nickel, copper, and iron, in the depolarizer layer of two layer systems were also evaluated. These were further studied by changing the compositions of the mixes. The compositions are given in Appendix B.

Manufacturing Methods.

The purpose of this study is to evaluate effects of variations of treatments of the components of the powder mixes. Figure D-1 gives a

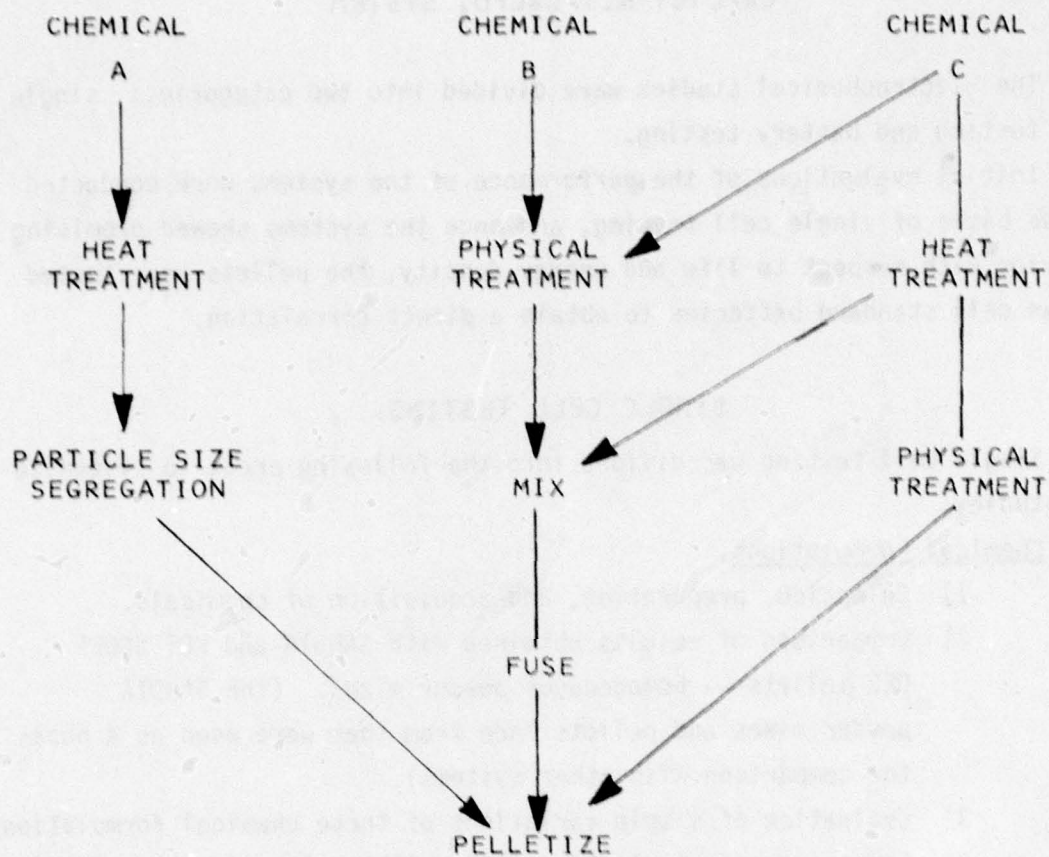


Figure D-1. Process Study Flow Diagram

process flow diagram for a typical three component (salt, CaCrO_4 , and Cab-o-Sil) system to form a powder mix. The variables are: treatment temperatures and times, effects of impurities, batch size, particle size distribution, and any other physical or chemical treatment applicable.

Powder mixes WPH-4 and WPH-6 have the same composition except that they were processed differently. In the WPH-6 system, Ca(OH)_2 was fused with KCl and LiCl eutectic before mixing with CaCrO_4 and Cab-o-Sil; whereas, Ca(OH)_2 was mixed with LiCl-KCl eutectic salt, CaCrO_4 , and Cab-o-Sil, and then fused in the WPH-4 system.

The major portion of this section is concentrated in the area of electrochemical studies dealing with the $\text{Ca/LiCl-KCl/CaCrO}_4$ system. Once studies were concluded with this system, efforts were directed to other systems. The bulk of the electrochemical studies was conducted on single cells.

In order to reduce variables to a practical testing level, only one homogeneous powder mix (WPH-2) was used to establish optimum parameters such as temperature, pressure, pellet thickness, pellet density, particle size, mixing methods, compositions, and additives. Peak voltage, life to 80% and 75% of peak voltage, and internal resistance were recorded using equipment described in Appendix A. The best results were then compared to other homogeneous powder mixes, where relative concentrations of mix ingredients were varied. The variations were limited to overall binder content, electrolyte (E) to depolarizer (D) ratio, and to the addition of various other chemicals to the mixes. These subsequent tests were performed at constant temperature and pressure parameters established during the initial WPH-2 testing.

The physical parameters of temperature, pressure, pellet density, pellet thickness, and particle size significantly affect the electrochemical characteristics of the system. The effect of temperature and pressure is graphically represented in Figure D-2. Although temperature and pressure are very critical for optimum performance, performance over a wide temperature range is ideal when the pressure is 10.34 psi.

The effects of pellet density and pellet thickness are shown in Figures D-3 and D-4, and the data is given in Tables D-1 and D-2

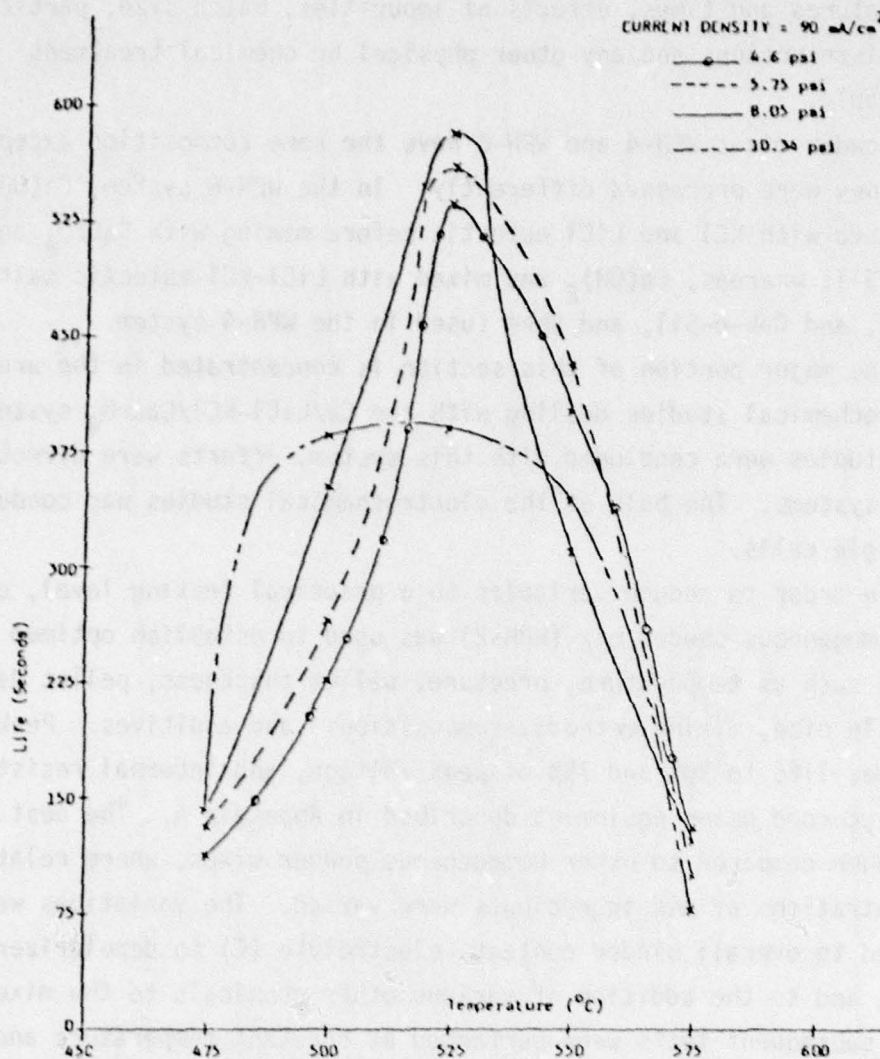


Figure D-2. Life Vs. Temperature for WPH-2 (Ca/LiCl-KCl/CaCrO₄) System at Different Pressures

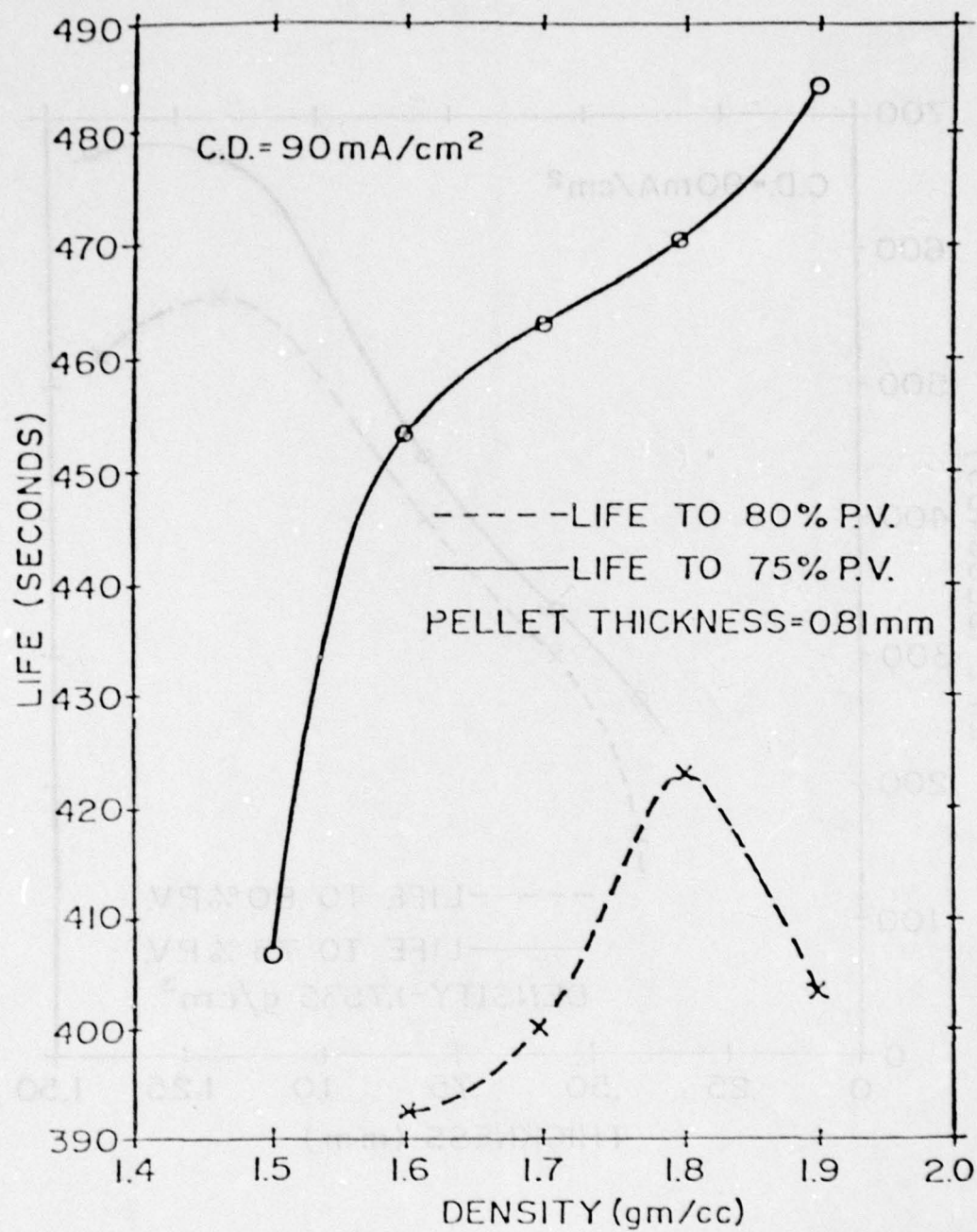


Figure D-3. Effect of DEB Pellet Density on Life
for Ca/LiCl-KCl/CaCrO₄ System

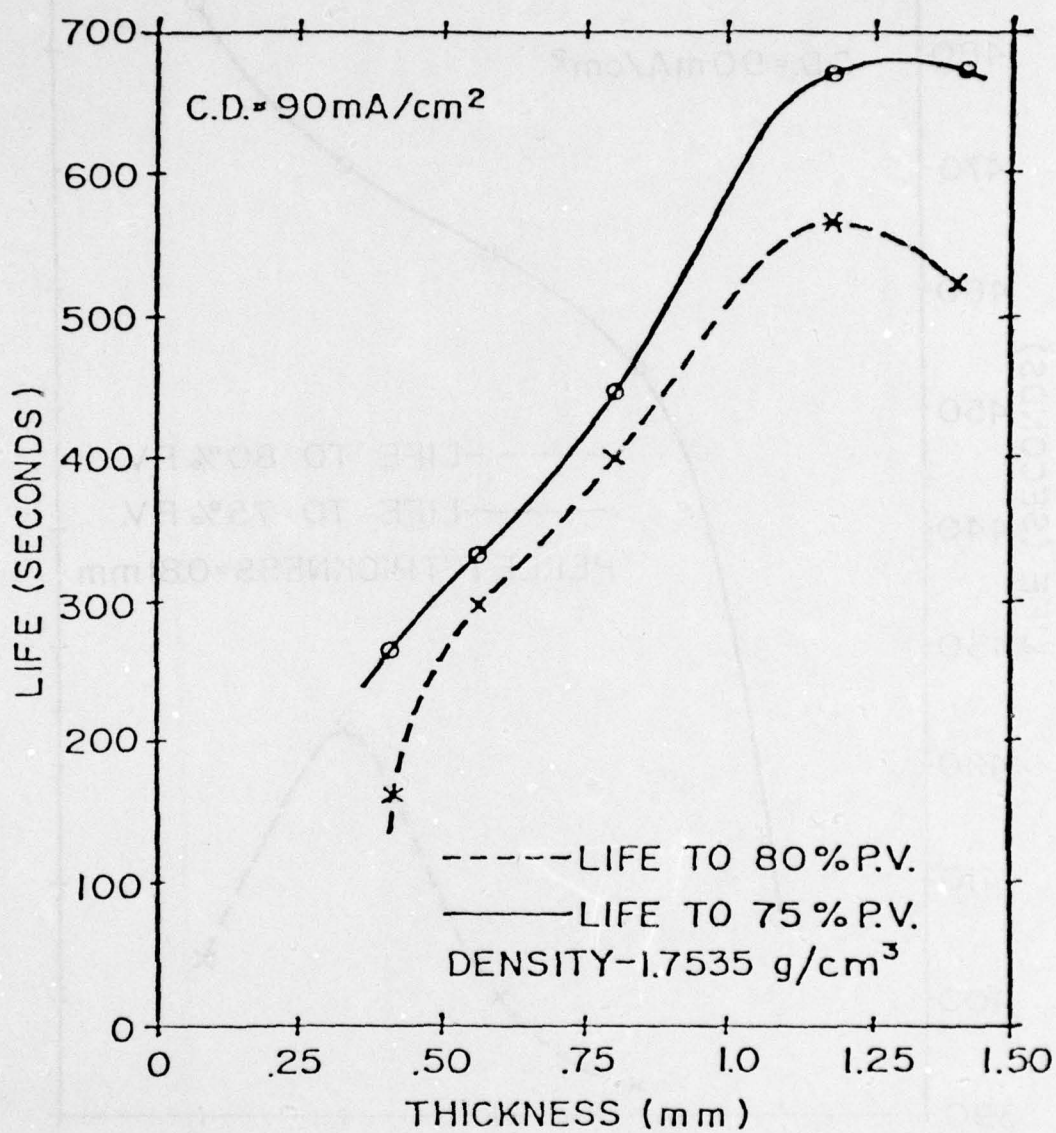


Figure D-4. Effect of DEB Pellet Thickness on Life
for Ca/LiCl-KCl/CaCrO₄ System

TABLE D-1

EFFECT OF DENSITY ON LIFE AT CONSTANT THICKNESS
IN SINGLE CELL TESTS

SYSTEM	O.C.V.	P.V.	LIFE TO 2.0 V	LIFE TO 1.8 V	r_1	r_2	#SHORTS/ #TESTS	REMARKS
WPH-2B1	3.141	2.43	355.3	406	0.585	0.969	0/10	Quiet
WPH-2C1	3.186	2.45	392.0	453	0.600	0.971	0/10	Quiet
WPH-2F1	3.149	2.454	400.0	463	0.566	0.978	0/20	Quiet
WPH-2G1	3.179	2.526	424.0	470	0.517	0.965	2/8	Slight Noise
WPH-2J1	3.162	2.390	404.0	484	0.646	1.000	0/9	Quiet

Thickness (mils) 1 = 32

Pressure = 4.89 psi

Temperature = 525°C

Current Density = 90 mA/cm²

Density (gm/cc) B = 1.5

C = 1.6

F = 1.7

G = 1.8

J = 1.9

 r_1 = Internal resistance at
beginning of test r_2 = Internal resistance at
1.6 volts

TABLE D-2

EFFECT OF THICKNESS ON LIFE AT CONSTANT DENSITY
IN SINGLE CELL TESTS

SYSTEM	O.C.V	P.V.	LIFE TO 2.0 V	LIFE TO 1.8 V	r ₁	r ₂	#SHORTS/ #TESTS	REMARKS
WPH-2A1	2.9	2.387	398.7	443.4	0.430	0.659	0/3	Quiet
WPH-2A2	2.964	2.438	561.4	664.0	0.431	0.950	0/5	Quiet
WPH-2A5	3.017	2.340	159.0	258.0	0.578	-	9/10	Considerable Noise
WPH-2A6	3.169	2.439	294.0	329.0	0.599	0.965	1/10	Quiet
WPH-2A7	3.127	2.490	513.0	676.0	0.511	0.958	0/10	Slight Fluctuation at 1.8 v

Current Density = 90 mA/cm²

Temperature = 525°C

Pressure = 4.89 psi

A denotes density = 1.7535 g/cc

1 denotes thickness = 0.032 inches

2 denotes thickness = 0.046 inches

5 denotes thickness = 0.016 inches

6 denotes thickness = 0.022 inches

7 denotes thickness = 0.055 inches

respectively. For WPH-2 powder mixes, the optimum performance was achieved when the pellet thickness was 0.8 mm and the pellet density was 1.8 g/cc. Beyond a pellet thickness of 1.2 mm, single cell life did not improve and an increase in cell resistance was seen.

The effects of particle size on battery performance were studied by making pellets in which mix particle sizes varied little within one pellet, and by making pellets in which mix particle sizes were varied over a given range. The results of tests at average current densities of 50 mA/cm² and 90 mA/cm² are given in Figure D-5. It was found that particle size affected both battery performance and pelletization. Large particles in the mix caused difficulties in forming pellets, and small particles caused flow problems in the automatic feed press. Although these problems posed no mechanical difficulties, it was found that a particle size distribution of -80 to +170 U.S. Standard mesh size was optimal for electrochemical performance and caused no pelletization problems.

Mixing problems become acute when the percentage of Cab-o-Sil was high. It was found, as suggested by Sandia Laboratories, that freon blending was the best mixing method when mixes high in binder content were used. The homogeneity of these mixes was determined by using a differential scanning calorimeter, and subsequent cell tests showed that lives remained within 2% of the mean. Pellets made from WPH-2 mixes blended by the freon method showed lives of 970 seconds at 50 mA/cm², about a 12% improvement over the life of pellets made by employing a V-blender for mixing. Latter pellets showed a life of 858 seconds at 50 mA/cm². Ball milling was a third mixing alternative, but was found to be too slow for the number of batches to be processed.

To obtain the best composition for this system, the composition of homogeneous powder mixes was varied, both with respect to the relative concentrations of electrolyte, depolarizer, and binder, and to the relative concentrations of additives to fixed amounts of homogeneous powder ingredients. Mixes were made up which had 4, 7, 10, and 12.5 percent of binder by weight and E/D ratios of 1.5:1, 1.65:1, and 1.8:1. Twelve mixes were subsequently evaluated at three different test loads, incorporating the effect of current densities on the

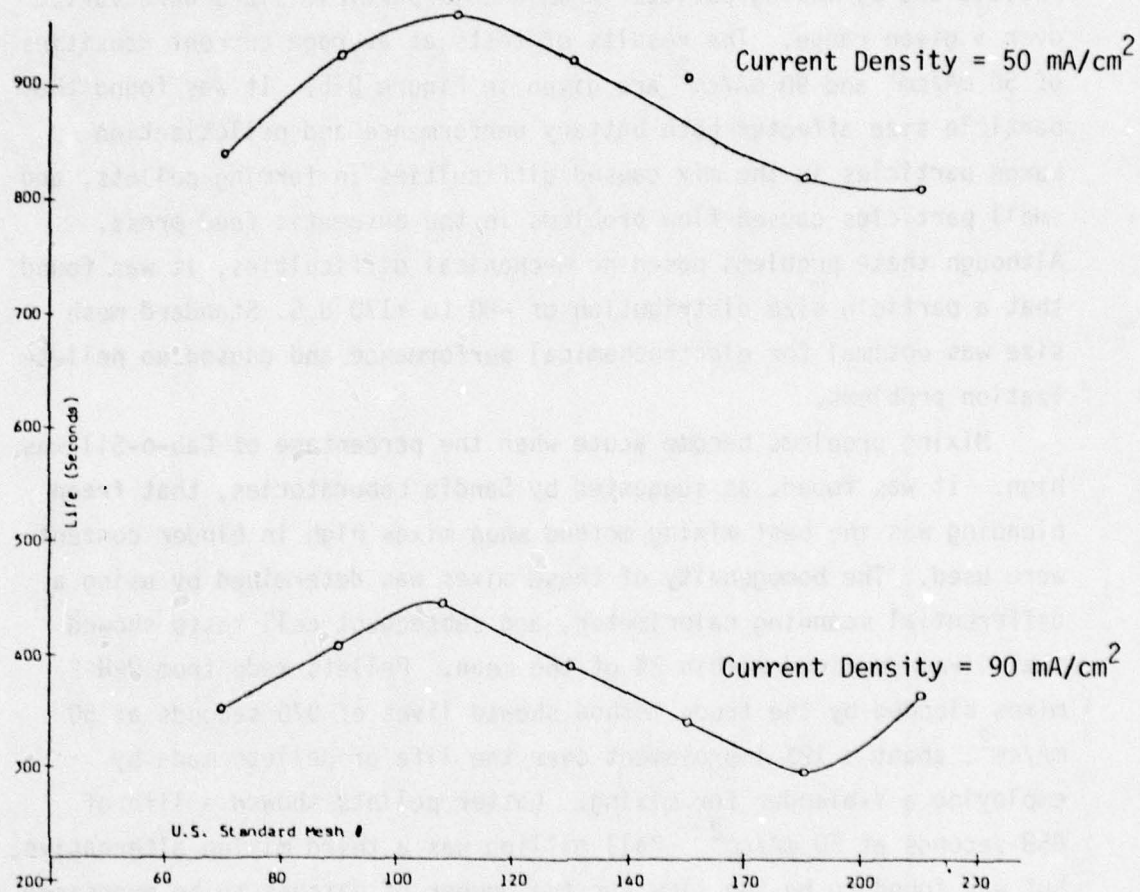


Figure D-5. Life Vs. Particle Size for WPH-2 (Ca/LiCl-KCl)/CaCrO₄

performance of the systems. The results of these tests at the various current densities are shown in Tables D-3, D-4, and D-5, and in Figures D-6 through D-11. The performance of the cells depended more on binder content and current density than on the ratio of electrolyte to depolarizer. At current densities of 50, 90, and 300 mA/cm², the shape of the life versus E/D ratio curves reversed between 7% and 10% binder content as shown in Figures D-6, D-7, and D-8. Thus, at binder content between 7% and 10%, the cell life becomes independent of the E/D ratio.

From Figures D-9, D-10, and D-11, it can be seen that at a low current density of 50 mA/cm², cell life is longest at Cab-o-Sil content of 12.5%. At high current density; i.e., 300 mA/cm², a lower binder content provides the longest life. A slight variation in E/D ratio is not critical at a current density of 300 mA/cm² but could be detrimental to cell life at 50 mA/cm².

The highest energy density of 128.5 Whr/kg was achieved with the WPH-11 system at low current density and with a Cab-o-Sil content of 12.5%. The next highest energy density was achieved from WPH-8, a mix which had 7% Cab-o-Sil. At 90 mA/cm², the WPH-2 mix containing 10% Cab-o-Sil had the highest energy density of 99.15 Whr/kg, and at 300 mA/cm², the WPH-9 mix containing 4% Cab-o-Sil showed the highest energy density of 88.15 Whr/kg. In conclusion, high energy densities could be obtained at low current densities in single cell tests, although this was not true in batteries. It is important to note that different mixes are desirable for operation at different current densities. The current density for the battery for which these experiments were conducted was 90 mA/cm². Consequently, the optimal mix was WPH-2, and further work was done with this mix only.

In an attempt to further optimize the performance of WPH-1, Ca(OH)₂, CaCl₂, K₂CrO₄, CrO₃, graphite, copper, and iron were used as additives in both single and two layer pellets. Peak voltage, life, alloy formation, and electrical noise were considered in single cell testing. The results at the three current densities are given in Tables D-6, D-7, and D-8.

Ten percent CaCl₂ was added to the electrolyte of WPH-2, improving the performance at current densities of 90 and 50 mA/cm². At 90 mA/cm²

TABLE D-3

SINGLE CELL TEST RESULTS FOR HOMOGENEOUS
SINGLE LAYER PELLETS AT 50 mA/cm² CURRENT DENSITY

SYSTEM	E/D	Cab-o-sil	PEAK VOLTAGE	LIFE TO 75% P.V.	ENERGY DENSITY
		(%)	(volts)	(sec.)	(Whr/Kg)
WPH-14	1.50	4	2.60	809	90.75
WPH-9	1.65	4	2.55	844	91.10
WPH-18	1.80	4	2.69	686	82.37
WPH-1	1.50	7	2.59	836	93.06
WPH-8	1.65	7	2.69	1013	121.64
WPH-17	1.80	7	2.76	665	84.06
WPH-10	1.50	10	2.60	939	105.34
WPH-12	1.63	10	2.59	801	89.17
WPH-2	1.80	10	2.62	970	110.48
WPH-11	1.50	12.5	2.67	1086	128.48
WPH-13	1.63	12.5	2.55	1087	117.30
WPH-7	1.80	12.5	2.50	1164	120.74

TABLE D-4

SINGLE CELL TEST RESULTS FOR HOMOGENEOUS
SINGLE LAYER PELLETS AT 90 mA/cm² CURRENT DENSITY

SYSTEM	E/D	Cab-o-Sil	PEAK VOLTAGE	LIFE TO 75% P.V.	ENERGY DENSITY
		(%)	(volts)	(sec.)	(Whr/Kg)
WPH-14	1.50	4	2.40	476	90.99
WPH-9	1.65	4	2.39	500	94.80
WPH-18	1.80	4	2.40	423	80.87
WPH-1	1.50	7	2.35	435	79.73
WPH-8	1.65	7	2.35	449	82.30
WPH-17	1.80	7	2.37	429	79.97
WPH-10	1.50	10	2.39	502	95.17
WPH-12	1.63	10	2.37	461	85.93
WPH-2	1.80	10	2.35	541	99.15
WPH-11	1.50	12.5	2.30	147	25.81
WPH-13	1.63	12.5	2.33	118	21.27
WPH-7	1.80	12.5	2.33	112	20.17

TABLE D-5

SINGLE CELL TEST RESULTS FOR HOMOGENEOUS
SINGLE LAYER PELLETS AT 300 mA/cm² CURRENT DENSITY

SYSTEM	E/D	Cab-o-Sil	PEAK VOLTAGE	LIFE TO 75% P.V.	ENERGY DENSITY
		(%)	(volts)	(sec.)	(Whr/Kg)
WPH-14	1.50	4	2.09	144	83.51
WPH-9	1.65	4	2.07	155	88.15
WPH-18	1.80	4	1.75	144	58.54
WPH-1	1.50	7	1.85	88	40.00
WPH-8	1.65	7	1.80	119	51.19
WPH-17	1.80	7	1.82	106	46.62
WPH-10	1.50	10	1.90	24	11.51
WPH-12	1.63	10	2.01	23	12.32
WPH-2	1.80	10	1.97	30	15.47
WPH-11	1.50	12.5	1.91	14	6.78
WPH-13	1.63	12.5	1.97	18	9.28
WPH-7	1.80	12.5	1.80	8	12.03

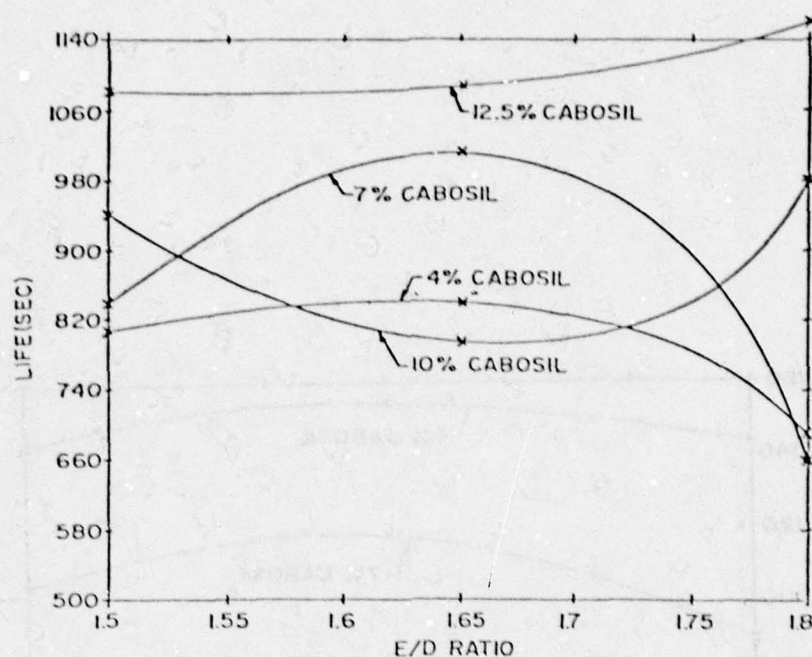


Figure D-6. Effect of $\text{LiCl-KCl(E)}/\text{CaCrO}_4\text{(D)}$ Ratio on Life for Different Cab-o-Sil(B) Levels at $50\text{mA}/\text{cm}^2$ Current Density

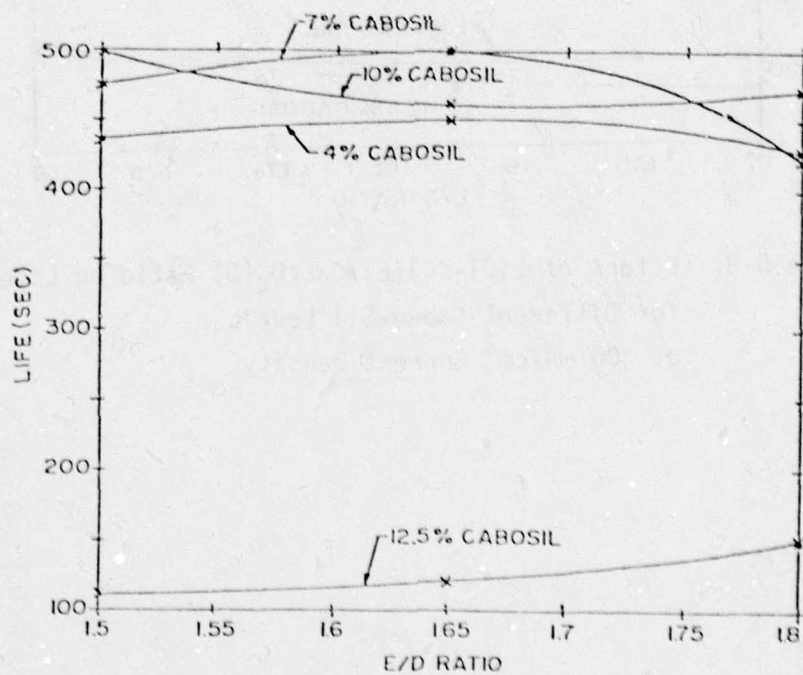


Figure D-7. Effect of $\text{LiCl-KCl(E)}/\text{CaCrO}_4\text{(D)}$ Ratio on Life for Different Cab-o-Sil(B) Levels at $90\text{mA}/\text{cm}^2$ Current Density

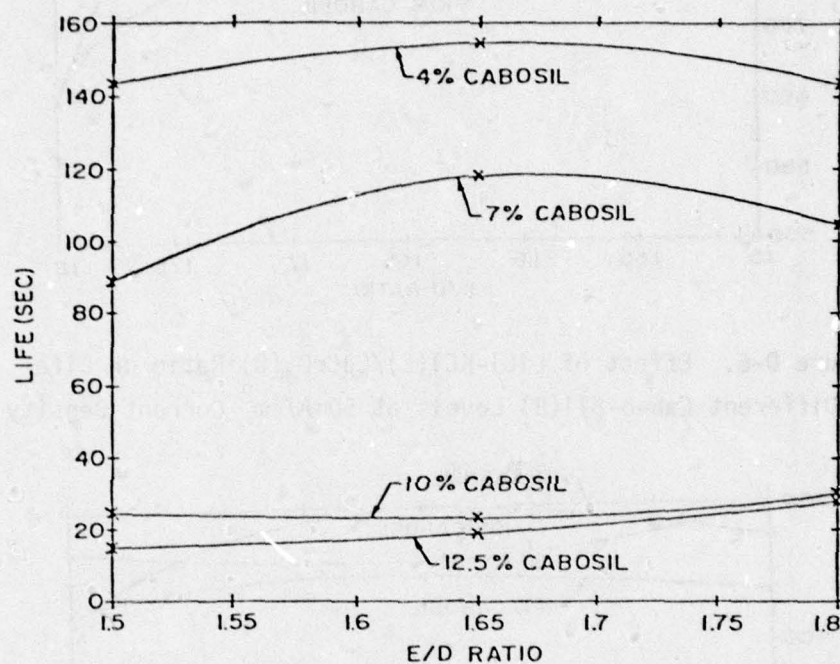


Figure D-8. Effect of $\text{LiCl-KCl(E)}/\text{CaCrO}_4\text{(D)}$ Ratio on Life for Different Cab-o-Sil Levels at 300 mA/cm^2 Current Density

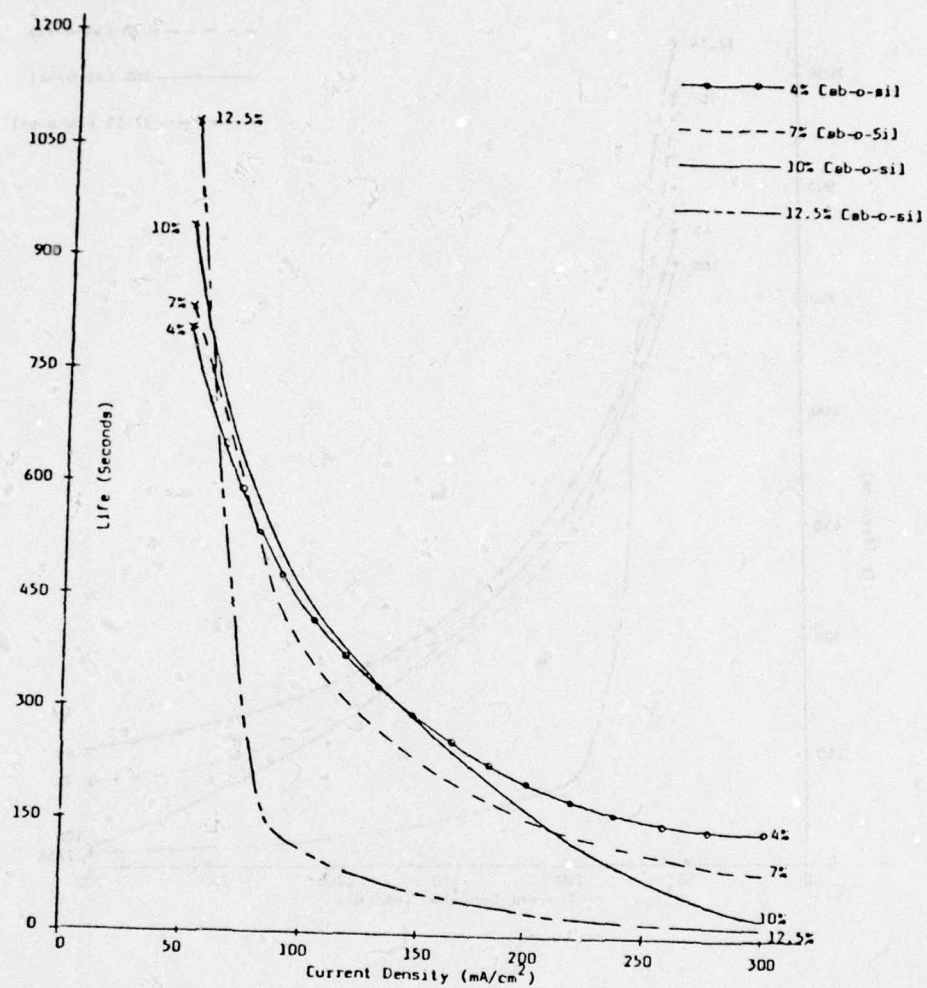


Figure D-9. Life Vs. Current Density for Ca/LiCl-KCl/CaCrO₄ Systems with E/D Ratio of 1.5:1

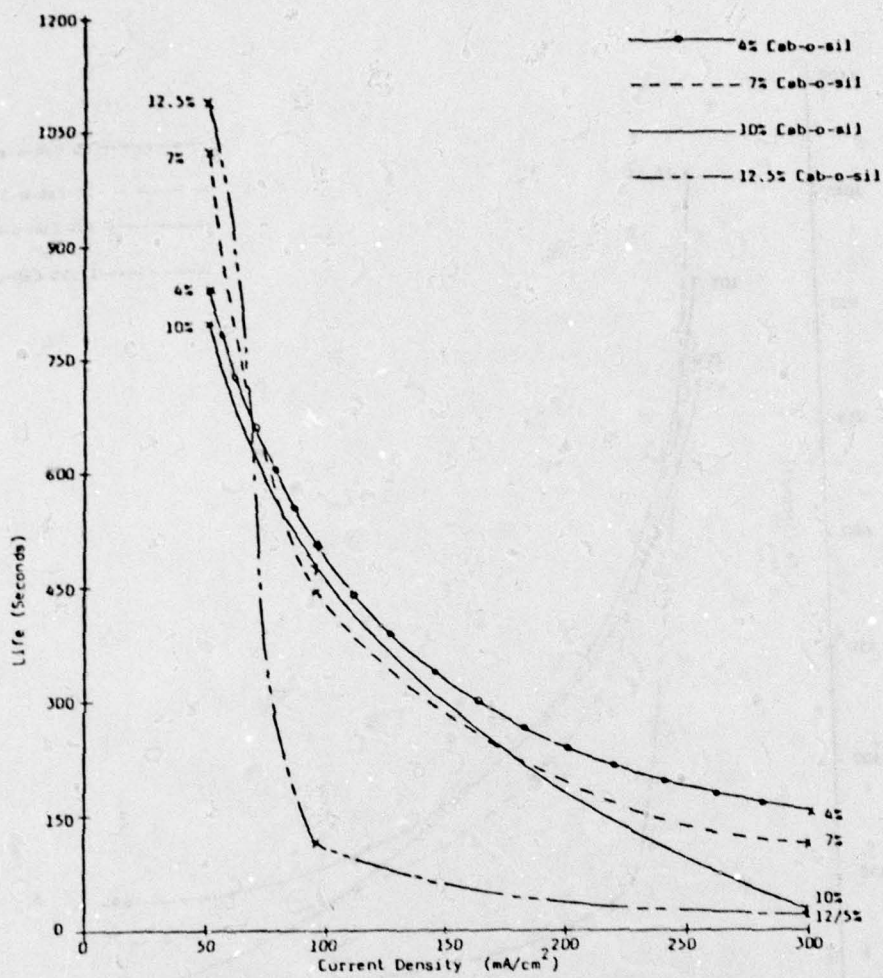


Figure D-10. Life Vs. Current Density for $\text{Ca/LiCl-KCl/CaCrO}_4$ Systems with E/D Ratio of 1.65:1

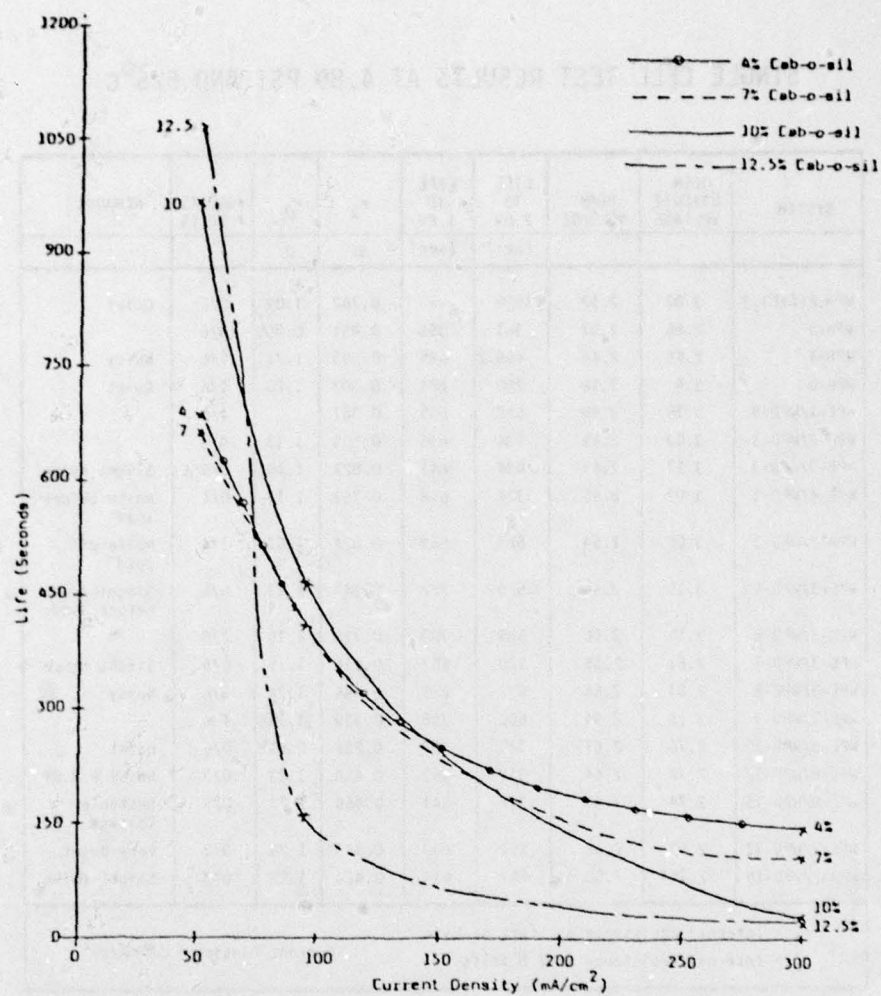


Figure D-11. Life Vs. Current Density for Ca/LiCl-KCl/CaCrO₄ Systems with E/D Ratio of 1.8:1

TABLE D-6

SINGLE CELL TEST RESULTS AT 4.89 PSI AND 525°C

SYSTEM	OPEN CIRCUIT VOLTAGE	PEAK VOLTAGE	LIFE TO 2.0V (sec)	LIFE TO 1.8V (sec)	r_1 Ω	r_2 Ω	#SHORTS # TESTS	REMARKS
WPH-2(CaCl ₂)	3.07	2.58	1520	-	0.762	1.09	0/6	Quiet
WPH-3	2.86	2.57	361	395	0.451	0.900	3/6	
WPH-4	2.68	2.44	498.2	585	0.393	1.21	1/6	Noisy
WPH-5	3.4	3.16	780	884	0.303	1.20	1/6	Quiet
WPE-1/WPD-9	3.16	2.89	622	665	0.367		1/6	
WPE-2/WPD-3	3.03	2.69	534	695	0.505	1.13	0/3	
WPE-3/WPD-3	3.17	2.63	634	841	0.821	1.18	0/6	Slight noise
WPE-4/WPD-3	3.02	2.55	374	658	0.751	1.13	0/4	Noise before load
WPH-2/WPD-3	3.06	2.54	523	569	0.824	1.67	1/4	Noise off load
WPE-3/WPD-5	3.10	2.56	520	722	0.844	1.13	0/6	Slight noise before load
WPE-3/WPD-6	3.15	2.66	589	703	0.728	1.18	2/6	
WPE-3/WPD-7	2.81	2.55	520	651	0.416	1.15	0/6	Slight noise
WPE-3/WPD-8	2.87	2.56	627	829	0.484	1.24	3/6	Noisy
WPE-3/WPD-9	3.18	2.94	660	758	0.329	1.156	4/6	
WPE-3/WPD-10	2.76	2.615	320	407	0.222	0.511	0/6	Quiet
WPE-8/WPD-12	2.72	2.44	315	462	0.458	1.29	0/3	Noise @ 2.0V
WPE-8/WPD-15	2.74	2.45	317	441	0.469	1.27	0/3	Unstable Voltage
WPE-2/WPD-11	2.93	2.58	551	637	0.543	1.29	0/3	Very quiet
WPH-2/WPD-15	2.764	2.50	697	814	0.422	1.22	0/3	Slight noise

r_1 = Internal Resistance at Start of Life
 r_2 = Internal Resistance at 1.8 Volts
Current Density = 50 mA/cm²

TABLE D-7

SINGLE CELL TEST RESULTS AT 4.89 PSI AND 525°C

SYSTEM	OPEN CIRCUIT VOLTAGE	PEAK VOLTAGE	LIFE TO 2.0V (sec)	LIFE TO 1.8V (sec)	r ₁ Ω	r ₂ Ω	# SHORTS # TESTS	REMARKS
WPH-2(CaCl ₂)	2.98	2.45	406	710	0.465	0.67	0/6	Quiet
WPH-3	2.89	2.38	227	254	0.428	0.840	3/6	
WPH-5	3.395	3.06	368	459	0.219	1.1	1/6	Quiet
WPH-4	2.66	2.32	313	380	0.293	0.980	4/9	
WPE-1/WPD-3	3.03	2.24	234	407	0.554	1.01	3/6	
WPE-2/WPD-3	3.04	2.46	197	349	0.473	0.893	0/10	Noise before & after load
WPE-3/WPD-3	3.09	2.3	178	360	0.687	0.9	6/25	
WPE-4/WPD-3	3.01	2.44	184	334	0.467	0.9	2/10	
WPH-2/WPD-3	2.913	2.343	145	222	0.487	1.22	1/5	Noise before load
WPE-3/WPD-5	3.12	2.46	227	356	0.54	0.89	0/10	
WPE-3/WPD-6	3.15	2.47	242	340	0.55	0.91	0/10	
WPE-3/WPD-7	2.72	2.37	185	309	0.295	0.86	1/10	
WPE-3/WPD-8	2.754	2.49	154	253	0.212	0.82	2/10	Noisy
WPE-3/WPD-9	3.20	2.79	228	351	0.296	0.925	4/10	
WPE-3/WPD-10	2.78	2.43	175	229	0.293	0.652	2/10	
WPE-8/WPD-12	2.75	2.31	98	159	0.378	1.14	0/3	Noise at 2V level
WPE-8/WPD-15	2.73	2.28	80	151	0.395	1.14	0/3	Voltage unstable
WPH-2/WPD-11	2.96	2.45	134	307	0.416	0.99	0/3	Quiet
WPH-2/WPD-15	2.80	2.39	335	421	0.350	0.88	1/9	Very slight Noise

r₁ = Internal Resistance at Start of Life
r₂ = Internal Resistance at 1.6 Volts
Current density = 90mA/cm²

TABLE D-8

SINGLE CELL TEST RESULTS AT 4.89 PSI AND 525°C

SYSTEM	OPEN CIRCUIT VOLTAGE	PEAK VOLTAGE	LIFE TO 2.0V (sec)	LIFE TO 1.8V (sec)	LIFE TO 1.6V (sec)	r ₁ Ω	r ₂ Ω	#SHORTS # TESTS	REMARKS
WPH-3	2.88	1.71	-	-	13			1/5	
WPH-4	2.67	1.98	-	-	12			1/6	
WPH-5	3.40	2.56	5.8	20.4	28.6	0.165	0.384	1/6	Quiet
WPE-1/WPD-3	3.05	2.00	-	17.7	23.8	0.264	0.327	1/4	
WPE-2/WPD-3	3.05	2.00	-	38.7	61.0	0.261	0.269	0/3	Noise after load
WPE-3/WPD-3	3.17	1.72	-	-	21.2			0/5	
WPE-4/WPD-3	3.03	1.98	-	27.0	61.0	0.265	0.275	0/3	
WPE-2/WPD-3	3.07	1.93	-	5.3	11.3	0.293	0.33	0/4	
WPE-3/WPD-5	3.15	2.14	15.1	50.0	79.3			0/6	
WPE-3/WPD-6	3.15	2.08	8.0	32.7	67.3			0/6	
WPE-3/WPD-7	2.77	2.04	12.3	52.4	73.8			1/6	Clean
WPE-3/WPD-8	2.88	2.08	14.2	53.3	80.9			0/6	Noise
WPH-2/WPD-10	2.8	2.0	-	6.0	10.0	0.2	0.357	0/3	
WPH-2/WPD-11	2.96	1.99	-	6.7	17.1	0.243	0.356	0/3	
WPH-2/WPD-12	2.72	1.81	-	1.0	4.0	0.249	0.306	0/3	
r ₁ = Internal Resistance at Start of Life r ₂ = Internal Resistance at 1.6 Volts Current Density = 300 mA/cm ²									

the cell life increased from 541 seconds to over 700 seconds at an energy density of 131.56 Whr/kg. At 50 mA/cm², the cell life increased from 970 seconds to 1534 seconds at an energy density of 141.68 Whr/kg. WPH-2 with a 10% CaCl₂ additive has been found to be the best Ca/LiCl-KCl/CaCrO₄ system so far. Li₂CrO₄ and CrO₃ increased the peak voltages on load, but did not improve cell life. K₂CrO₄ decreased the peak voltage and Ca(OH)₂ caused electrical noise and alloying. Formation of alloys and subsequent shorts were negligible in all other tests, however. Lastly, the metallic additives showed no improvement in cell performance.

Similar experiments involving two layer pellets produced different results. Two layer pellets were made which had the same weight and thickness as the single layer homogeneous pellet. In studying the effect of the E/D ratio on the performance of the two layer pellet at current densities of 50, 90, and 300 mA/cm², it was found that this ratio was critical at high current densities. At 50 and 90 mA/cm² the cell performance was virtually unaffected. These results are illustrated in Figure D-12. The experiments with additives showed little or no improvement in cell performance when compared to WPH-2 with CaCl₂. Homogeneous pellets appeared to produce the best results for long life applications at 90 mA/cm². This is not necessarily true for other catholytes or for systems requiring short lives with high current drain.

BATTERY TESTING

Batteries with standard size cells of 38 mm diameter were made for direct correlation with single cell tests. Subsequently, batteries with 61 mm diameter cells were made, the design goal being to produce even larger batteries which would produce 30 amperes at 90 mA/cm², with three paralleled stacks.

38 mm Diameter Cell Batteries.

Approximately 150 Ca/LiCl-KCl/CaCrO₄ batteries with standard 38 mm diameter cells were built, using both single layer homogeneous and two layer pellet systems and were tested at various current densities. In addition, studies were made in the pyrotechnical aspects of battery operation. Both heat paper, consisting of Zr and BaCrO₄, and heat

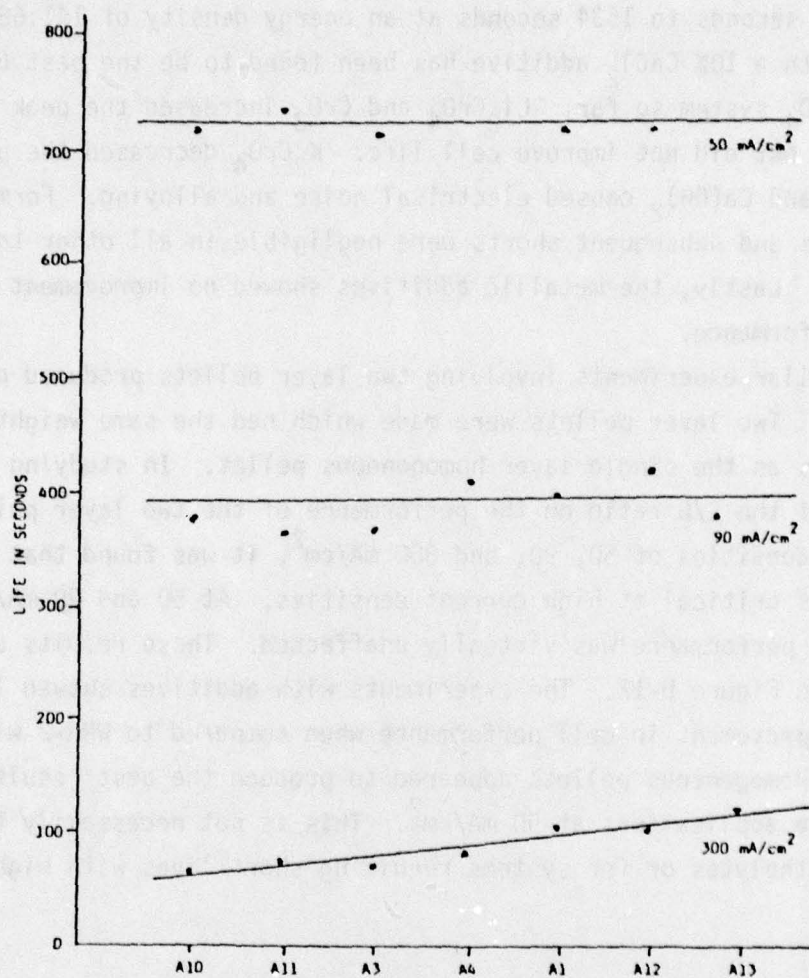


Figure D-12. Effect of EB:DB Ratio on Life of Two Layer Pellet
(Ca/LiCl-KCl/CaCrO₄ System)

pellets, made from a mixture of Fe and KClO_4 (86:14 w/o), were used as a pyrotechnic and these results are discussed in detail in Appendix E of this report.

Results from battery tests using standard size cells indicated that the WPH-2 pellet mix produced the most desirable results. The best batteries of this group, S/N WPO-43 and S/N WPO-44, Table D-9, achieved an average life of 2.7 minutes and an energy density of 4.3 Whr/kg at the temperature extremes tested. The results of these battery tests, including several powder mixes, using heat paper, heat pellets, different pressures and tests at the three current densities have been discussed in interim reports.

61 mm Diameter Cell Batteries.

Batteries with 61 mm diameter cells using $\text{Ca/LiCl-KCl/CaCrO}_4$ systems were also built and tested at different current densities. At a current density of 90 mA/cm^2 , a life of 4.5 minutes and 15.4 Whr/kg energy density was produced by the $\text{Ca/LiCl-KCl/CaCrO}_4$ battery (S/N P-17). A life of over 16 minutes was achieved using this system (S/N 3831) indicating that this system is capable of sustaining a long thermal life. At 48 mA/cm^2 , the energy density of $\text{Ca/LiCl-KCl/CaCrO}_4$ battery S/N P-18 was improved to 13.3 Whr/kg and the life extended to 9.4 minutes. The results of the batteries achieving the best performance are given in Table D-10.

TABLE D-9

BATTERY TEST RESULTS FOR VARIOUS $\text{Ca/LiCl-KCl/CaCrO}_4$ SYSTEMS
USING 38 mm OD CELLS

BATTERY NO.	BATTERY CONDITION	PEAK VOLTAGE	RISE TIME	LIFE	SYSTEM	REMARKS
	$^{\circ}\text{C}$		(ms)	(sec)		
WP-035	-40	25.0	370	127	WPE-3/WPD-3	
WP-037	+70	24.9	280	121	WPE-3/WPD-3	
WP-043	-40	25.7	570	161	WPH-2	4.3Whr/Kg
WP-044	+70	25.2	370	164	WPH-2	4.3Whr/Kg
WP-047	-40	25.2	430	169	WPH-4	
WP-048	+70	25.2	420	80	WPH-4	
WP-086	-40	30.0	290	213	WPH-5	
WP-088	+70	28.0	200	70	WPH-6	
WP-114	-40	25.5	400	11	WPE-3/WPD-7	
WP-116	+70	25.3	350	77		
LOAD = 20.0 Ω LIFE MEASURED TO 18 VOLTS						

TABLE D-10

BATTERY TEST RESULTS FOR Ca/LiCl-KCl/CaCrO₄ SYSTEM
 AT DIFFERENT CURRENT DENSITIES
 (61 mm DIAMETER CELL BATTERY)

SYSTEM	S/N	TEMP °C	CURRENT DENSITY (mA/cm ²)	PEAK VOLTAGE (Avg.)	LIFE TO 75% P.V. (Min.)	STACK ENERGY DENSITY (Whr/kg)
Ca/LiCl- KCl/CaCrO ₄	P-14	-40	90	26.7	3.8	13.3
	P-16	+70	90	26.7	2.6	8.8
	P-17	+23	90	26.7	4.5	15.4
Ca/LiCl- KCl/CaCrO ₄	P-18	+23	48	27.2	9.4	13.3
	P-20	+23	16	28.2	11.1	9.4
	3831	+23	9	19.0	16.0	5.9

APPENDIX E

NON-STANDARD TECHNIQUES

FUSIBLE HEAT RESERVOIRS

Fusible heat reservoirs have the advantage of providing heat at a pre-determined temperature. They are "thermally timed" sources in which the activation temperature and amount of heat released can be varied by changing the chemical compositions and weight.

An eutectic mixture of NaCl and Li_2SO_4 was made and blended with Cab-o-Sil in a ratio of 88:12 for future studies as a possible fusible heat reservoir.

DSC studies were made on this eutectic and certain off-mixtures to ascertain the thermal properties and solidus temperatures. The studies were along the following lines:

- 1) Choosing a chemical system for optimum performance at a high or low temperature only.
- 2) Studying the feasibility of manufacturing a fusible reservoir paper for use in the sidewall of a battery. Also, use of these reservoirs at appropriate stack positions.

Table E-1 gives the results of evaluations of different fiberglass tapes impregnated with eutectic mixture of sodium chloride-lithium sulfate at 500°C . It was found that ECCIIB was the most suitable tape for this purpose. This impregnated tape was tested for use in the outer can as a buffer reservoir.

For the stack, pellets made of this mixture of sodium chloride-lithium sulfate with Cab-o-Sil were used.

ELECTRICAL AND THERMAL TECHNIQUES

This task was directed toward electrical and thermal devices which might enhance overall battery performance. No experimental work was done in this area. However, several ideas worth looking into are suggested below.

To increase battery life, the following areas are suggested for investigation:

TABLE E-1

EVALUATION OF FIBERGLASS TAPES FOR
IMPREGNATING WITH $\text{NaCl-Li}_2\text{SO}_4$ BUFFER POWDER

TYPE OF TAPE	TAPE. WT. gm/in ²	AMT. SALT gm/in ²	Cal/in ²	RESPONSIVE CHARACTERISTICS
1) Columbia (Tight Weave)	.1218	.2365	22.25	Brittle
2) Columbia (Loose Weave)	.1114	.2980	28.04	Brittle
3) Burlington (Loose Weave)	.1162	.3466	32.61	Slightly flexible
4) Tight Weave Volan	.1211	.3093	29.10	Brittle
5) Burlington (1-3/4" wide, .005" thick)	.0725	.1793	16.87	Smooth and very flexible
6) Very Loose Weave (As received)	.1126	.2130	20.04	Improper wetting
7) Loose Weave Volan (As received)	.1344	.2387	22.46	Brittle
8) Tight Weave Volan (As received)	-	-	-	Broke down
9) Tight Weave Volan (Fired)	.1369	.3009	28.30	Smooth, brittle, good absorption
10) Tight Weave Volan (Fired)	.1343	.2610	24.56	Same as above
11) Tight Weave Volan (As rec'd.)	.1369	.2666	25.08	Smooth, brittle
12) Loose Weave Volan (Fired)	.1315	.3769	35.46	Smooth, flexible
13) Very Loose Weave (As rec'd.)	.1160	.3294	31.0	Very flexible, smooth
14) Loose Weave Volan (Fired)	.1320	.3504	32.97	Brittle
15) ECCIIB	.1241	.5648	53.14	Very flexible (dipped at 500°C, lumpy deposit)
16) ECCIIB	.1217	.4399	41.39	Very flexible and smooth

- 1) Stacks paralleled outside the battery. This will lower the heat generated within the battery and at the same time allow the use of buss bars to decrease the internal resistance drop.
- 2) Use of diodes to prevent one stack of the battery from acting as a load on other parallel stacks.
- 3) Use of voltage regulating devices to control designed-in over voltage.

To increase battery performance at high and low temperatures (i.e., to widen the operating temperature range of the battery), the following are suggested:

- 1) Squib systems that will be activated thermostatically and be used for supplying auxiliary heat when needed.
- 2) Squib systems that will be activated with a time delay circuit and used for supplying auxiliary heat at a critical point in life.

A market search has uncovered a pyrotechnic switch which may be activated by a thermostat, a voltage sensing circuit, or a timing circuit. This switch can be adapted for use in a thermal battery. At present, the most promising technique is the use of a voltage sensing device which would trigger either a secondary heat source or another battery stack to prolong battery operation.

PYROTECHNIC STUDIES

The pyrotechnic studies were based on the application of heat pellet technology; i.e., the use of heat pellets using a mixture of iron powder and potassium perchlorate.

Since heat paper made from $Zr + BaCrO_4$ was readily available, batteries were thermally balanced using this heat source. Later, the batteries were also balanced with heat pellets and a comparative study was conducted to determine the differences.

Based on the results of the tests of the batteries built using WPH-2 powder mixes and tested on a 20 ohms load, the following conclusions were drawn:

- 1) The heat paper batteries were faster activating than the heat pellet batteries.
- 2) The peak voltages were higher for pellet batteries than for heat paper batteries, but there was no discernable difference in performance.

- 3) The pressure requirement for heat pellet batteries was lower than for heat paper batteries. This pressure was responsible for faster or slower start times.
- 4) The heat pellet batteries were simpler to manufacture than were the heat paper batteries, since they require fewer parts and fewer assembly operations are involved.
- 5) The heat pellets were preferable for long life batteries where rigidity in shape and maintenance of stack pressure for optimum performance were desired. The pressure drops to almost zero for heat paper batteries.